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The Effect of Temperature and Exposure to X-Rays Upon Triboluminescence.

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IN a study[1, 2] made at the Institute for Radium Research in Vienna it was observed that triboluminescence[3] (TL) involves three distinct factors one or more of which may account for the TL of a given substance:

(a) Emission closely resembling phosphorescence and low temperature thermoluminescence which may be activated by exposure to radium. (*Emission a.*)

(b) Emission which is characteristic of the material and for which the only excitation is mechanical breaking. (*Emission b.*)

(c) Emission due to electric discharge in air the spectrum of which shows the nitrogen bands. (*Emission c.*)

The present paper describes further observations of TL in a number of materials including fluorite, sphalerite, kunzite, quartz and uranium nitrate. The materials under observation were exposed to x-rays at room temperature and the effect of this exposure upon the TL was observed and compared with the effect observed previously of exposure to radium. Exposures to x-rays were also made at liquid-air temperature to determine the way in which the energy stored from x-rays and released as TL was affected by a change in temperature of exposure. Observations of the TL of both exposed and unexposed materials were made by grinding them at various temperatures between that of liquid air and 60°C. In this way the effect of temperature upon both the storage of energy and the emission of this energy as TL was observed.

APPARATUS AND METHOD OF OBSERVATION

As a source of x-rays for this work a water-cooled tungsten target tube running on a voltage of about 55,000 and a current of 8 milliamperes was used. The wave-length was limited to from 0.5 to 0.7A by a filter of $\frac{1}{4}$ inch of oil and 0.2 mm of Celluloid. Specimens were exposed at room temperature at a distance of 6 cm from the filter and, at low temperatures, at a distance of 16 cm for periods varying from 15 to 30 minutes. Low temperature during exposure was maintained by fastening the materials under observation to the top of a heavy copper bar the lower part of which was immersed in liquid air in a Dewar flask, only the top projecting above the flask. The specimens were wrapped in Cellophane to keep them dry.

Observations of TL at room temperature were made when the material was ground in a glass mortar with a glass pestle. For observations at low temperature a porcelain mortar was used which was cooled by filling it with liquid air and allowing nearly all the air to evaporate before the specimen to be ground was dropped into the

[1] Frances G. Wick, Mitt. d. Inst. f. Radiumforschung No. 389, Wien. Ber. **11a**, 145, 689 (1936).
[2] Frances G. Wick, J. Opt. Soc. Am. **27**, 275 (1937).
[3] In this paper the abbreviations suggested by Imhof are used as follows: Triboluminescence—TL; triboluminescent—tl.

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bottom of the mortar. The grinding was done with a glass pestle which transmitted light. For observations above room temperature the mortar was placed in an agate cup surrounded by hot water which brought the specimen to a temperature of about 60°C. In all cases the mortars and pestles were tested to see that they themselves emitted no TL during the operation of grinding. In the case of crystals of considerable size observations were made of the TL emitted when they were crushed in a vice. When the intensity of emission permitted visual spectrum observations were made with a direct vision spectroscope of large light-gathering power with the slit illuminated by the light emitted when the specimen was ground in a mortar or crushed in a vice.

Fluorite

Natural fluorites are of special interest in the study of luminescence and much is known about the emission of light by these crystals under different types of excitation. They all show TL in the natural condition and are much more strongly tl after exposure to radium.[1, 2] In this work the effect of exposure to x-rays upon many specimens from different localities was observed and a special study was made of those specimens listed in Table I. In general the same changes in intensity of TL are produced by exposure to x-rays as those resulting from exposure to radium.[1, 2] TL, *Emission a*, is intensified by both of these agencies and it has the same color and spectral quality as a corresponding phosphorescence or thermoluminescence excited by the same source. Spectroscopic observations of emissions of light after exposure to x-rays by specimens 5, 8, 9, 13 and 14, Table I, show the same spectra in TL as those observed in the phosphorescence and thermoluminescence of the same specimens at a somewhat higher temperature. The spectra are easy to compare because of the sharp emission bands due to the rare earth impurities which are seen in all of these types of emission in the fluorite. The specimens enumerated all show the band of Tb, 5400–5500A and the band of Dy, 4500–5000A, the relative intensities of these bands differing in the specimens from different localities. From the study of these spectra it is evident that TL is definitely related to phosphorescence and thermoluminescence.

The Effect of Temperature of Exposure and of Grinding Different Substances

Some materials showing *Emission b* or *Emission c* are not changed in intensity of TL by exposure to x-rays at any temperature and there is no change in intensity of TL with a change in temperature of grinding. Sphalerite, barium chloride and zinc sulphide show no change in intensity of TL after exposure to x-rays at any temperature and the temperature of grinding makes no difference in the intensity of this emission. It is of interest to note that the color of the TL in all of these substances is orange or reddish and not the green which is characteristic of a discharge in air.

A number of substances including calcium tungstate, sulphate of quinine, quartz of different varieties, sugar and uranium nitrate which are not activated to TL perceptibly by exposure to x-rays show an increase in brightness of TL as the temperature of grinding is lowered the greatest brightness being at the lowest temperature observed, that of liquid air. There is a decrease in brightness as the temperature is raised to 60°C. In all of these cases it seems probable that at least a part of the TL is due to an electric discharge in air, *Emission c*. Recent investigations of Harvey[4] have shown that some substances which emit green TL when broken in air show red light when shaken in an atmosphere of neon since the discharge gives the color characteristic of an

Table I. *Fluorite.*

Number	Source
1	Alcorn, Tenn.
2	Axel Alpe, Pinzgau, near Salzburg.
3	Derbyshire, England. (dark purple)
4	Derbyshire, England. (yellow, opaque)
5	Florissant, Cal.
6	Franklin, N. J.
7	Hastings Co., Ontario.
8	Montrose, Cal.
9	Torrington, New South Wales.
10	Trumbull Co., Conn.
11	Washington.
12	Weardale, Durham, England. (blue-green)
13	Weardale, Durham, England. (purple)
14	Westmoreland, N. H.

[4] E. N. Harvey, Science **89**, 460 (1939).

electric discharge in nitrogen in the first case of a discharge in neon in the second. In some cases, however, such as uranium nitrate Harvey observed that the characteristic green color due to the luminescence of the material itself and the red color of the discharge in neon are both present. Evidently *Emission b* and *Emission c* are both present. The author observed that the TL of uranium nitrate—$6H_2O$ which is very strong at room temperature is much stronger at liquid-air temperature. The spectrum of the TL shows the bands characteristic of uranium luminescence and these are sharpened at low temperature. A clear crystal of uranium nitrate dropped into liquid air emits a scintillating light. Evidently the crystal is fractured by the sudden change of temperature and at each fracture light is emitted —possibly an electric discharge takes place upon fracture and this excites the uranium nitrate to luminescence. The same crystal can be repeatedly cooled and warmed with emission of light upon each cooling until the cracks in the crystal become so close that it begins to disintegrate. The increase in the intensity of the TL of quartz as the temperature is lowered is very marked. All varieties of quartz examined including clear quartz crystals from different localities, opaque white quartz, rose quartz and sea sand show this effect. Some of the specimens show brilliant light when ground or struck at liquid-air temperature. Quartz appears to fracture more easily at low temperatures increasing the intensity of TL because more fractures occur upon grinding or striking. Because the color of the TL of quartz is green it appears that a part, at least, of the TL may be due to a discharge in air.

Substances showing TL described as *Emission a* are excited to TL by exposure to x-rays. In general they are more strongly excited by exposure at liquid-air temperature than at room temperature. The temperature of grinding such substances also makes a difference in the intensity of TL. Specimens showing the temperature effects very strongly are fluorite, kunzite, tremolite, tourmaline and wollastonite. These materials all show tl maxima at certain temperatures, in some cases more than one such maximum. Each tl maximum is associated with a phosphorescence or thermoluminescence maximum of the same color and spectral quality. The tl maximum is always at a lower temperature than that of the corresponding phosphorescence or thermoluminescence maximum. Specimens of fluorite exposed to x-rays at liquid-air temperature bring out strikingly the relation of TL to phosphorescence and thermoluminescence. A number of fluorites, when they are warming up to room temperature after exposure to x-rays at liquid-air temperature, emit strong phosphorescence maxima of different colors at different temperatures. For each of these emissions of phosphorescence there is an emission of TL which may be observed at a temperature a little below that at which the phosphorescence appears. For example, purple fluorite from Weardale, Specimen 7, Table I, shows no phosphorescence at liquid-air temperature after exposure to x-rays at that temperature. As the specimen warms up a strong blue phosphorescence is emitted at a low temperature persisting through a narrow range. At a temperature considerably higher than this there is a strong yellow phosphorescence and at room temperature a strong green phosphorescence. TL of the same colors, blue, yellow and green can be observed by grinding the specimen at a temperature somewhat lower than that at which the phosphorescence of the corresponding color appears. From previous observations,[5] this Weardale fluorite is known to contain Eu in relatively large amount and Sm, Dy, Nd and Gd in smaller amounts as impurities. The maxima observed are due to the different rare earths. Other fluorites, upon warming up to room temperature after exposure to x-rays at liquid-air temperature, show different sequences of colors depending upon the impurities present in the crystals but in every case of emission of phosphorescence TL of the same color could be observed at a somewhat lower temperature. Observations previously made show that specimens which, with or without exposure to radium show thermoluminescence at a relatively low temperature emit TL of the same color at room temperature. In this case the TL bears the same relation to thermoluminescence as it does to phosphorescence emitted at a lower temperature. Because observations of TL have not been made above 60°C TL corresponding to the emission of

[5] Frances G. Wick, Phys. Rev. **24**, 272 (1924).

thermoluminescence at higher temperatures has not been observed.

Kunzite, after exposure to x-rays at liquid-air temperature has an orange colored phosphorescence with a maximum below room temperature, and at a somewhat lower temperature, a maximum TL of the same color. This material also has a green TL which is present at all temperatures and cannot be removed by heat. It is of interest that, in this case *Emission a* is orange and the second emission which may be classed as *b* or *c* is green.

Wollastonite resembles kunzite in that the color of the TL which appears at a certain low temperature after exposure to x-rays at liquid-air temperature is of one color, lemon yellow, and that emitted at all temperatures after the specimen has been heated is another color, green.

Activation of Luminescence by Mechanical Means

It is known from various observations that the breaking of a crystal constitutes a source of excitation not only of triboluminescence but also of phosphorescence and thermoluminescence. A number of specimens including blue-green fluorite from Weardale, England, No. 12, Table I and specimens of $CaSO_4$ activated by Mn which are phosphorescent after exposure to x-rays have the intensity of this phosphorescence increased when the material is ground in a mortar. When fluorites are heated on a hot plate with emission of thermoluminescence, at certain temperatures, the crystals fly to pieces with increase of brightness on breaking. The small pieces are definitely brighter than the large crystal was before it broke. This effect seems to be similar, at a higher temperature, to that observed in uranium nitrate when sudden fracture takes place upon dropping a crystal of this substance into liquid air. It is also known[1, 2, 6] that materials may be excited to thermoluminescence by the process of fracture. Fluorites and other crystals heated to red heat completely exhausting the effect of any source of excitation are made thermoluminescent by the process of grinding. This emission has been called "tribothermoluminescence."

[6] Nyswander and Cohn, Phys. Rev. **36**, 1257 (1930).

Discussion of Observations

It is of interest to attempt to interpret these results in the light of investigations of the mechanism of luminescence in solids recently summarized by Randall[7] and others. It is well known that most luminescent substances contain a small amount of impurity which functions as an activator and a much larger mass, usually crystalline, of another substance which acts as a diluent. In the case of the fluorites, the rare earths and manganese play the part of activators and calcium fluoride is the diluent. The chief problems to be solved are the function of the activator and the extent to which the whole crystal lattice is involved in the emission of luminescence. The study of TL may contribute some evidence as to the part played by each of these factors.

That the emission of luminescence in fluorite is closely associated with the activator atoms is indicated by the sharp, characteristic rare earth bands and, in some cases, the band of manganese previously observed[5, 8, 9] in different manifestations of luminescence in fluorite such as cathode and thermoluminescence, and more recently in TL.[1, 2] It has been pointed out by Randall[7] and others that the emission of these characteristic bands in a solid is due to the fact that the rare earths and manganese are distinguished by the possession of incomplete inner shells, the $3d$ and $4f$ shells, respectively. The rare earth bands in the fluorescence of fluorite are attributed to transitions within the $4f$ shell which is well shielded by the outer electrons so that the bands lose little of the sharpness they possess when the atoms are in the free state. The fact that substances like fluorite activated by a small amount of impurity are excited less by cathode rays than by x-rays is explained by Tomascheck[10] and Riehl[11] as given in a recent paper by Seitz.[12] The atoms of the impurity activator are far apart so that the bombarding cathode-ray electrons lose most of their energy in the bulk of the material, the diluent. For instance,

[7] J. T. Randall, Trans. Faraday Soc. **35**, 2 (1939).
[8] Frances G. Wick, J. Opt. Soc. Am. **21**, 223 (1931).
[9] Urbain, Comptes rendus **143**, 825 (1906).
[10] Tomascheck, Sitz. Ber. der Ges. Marburg **63**, 119 (1928).
[11] N. Riehl, Ann. d. Physik **29**, 636 (1937).
[12] F. Seitz, Trans. Faraday Soc. **35**, 74 (1939).

if the ratio of the number of luminescent centers due to atoms of activator to the number of atoms of diluent should be 10^{-4} the fraction of the energy absorbed from the cathode rays used in excitation of luminescence would be of the same order.

Luminescence, however, is not confined to the absorption of energy by impurity atoms since pure substances are known to be luminescent. Riehl[13] and others have shown that zinc sulphide exhibits a phosphorescence characteristic of its pure state. This is shown only after heat treatment such that the two crystal forms of the substance are present. The existence together of the two crystal types produces distortions within the lattices of both. It has been suggested that perturbed lattice points act as potentials attracting and repelling electrons. Ewles[14] and others have suggested that the function of an activator is to enter the lattice of the diluent and produce distortions and that these distortions play a large part in the phenomenon of luminescence. Distortions may produce the same effect as activating impurities. The idea that phosphorescence is associated with lattice distortions is supported by the observation of Ewles[14] that if a clear calcite crystal showing no fluorescence or phosphorescence is heated to 800°C in a stream of CO_2 and then suddenly cooled so as to produce thermal strains a phosphorescence lasting some minutes is observed. The fact that heat treatment[15] of many substances produces a marked effect upon the duration of phosphorescence may be explained by the distortion in the crystal lattice. The effect of pressure[8] upon fluorite and other crystals changes the excitation by a given exposure to radium and the subsequent emission of luminescence probably due to distortions in the crystal lattice. Tribothermoluminescence[1, 2, 6] may be interpreted as excitation due to lattice distortion. It is excited by purely mechanical means such as grinding a crystal in a mortar.

Substances belonging to the class which gives *Emission a* of which fluorite is an example show TL which is definitely associated with the activator atom. Exposure to radium or x-rays causes the displacement of electrons in certain energy levels. The mechanical energy supplied by the fracture or grinding causes the return of the electrons to their ground state with the emission of TL. This may also be caused by an increase of temperature producing in this case, either phosphorescence or thermoluminescence. For the emission of TL not so much rise in temperature is needed.[1, 2] It may be imagined that, when specimens of fluorite are exposed to x-rays at liquid-air temperature energy is absorbed by the rare earth atoms. Electronic transitions occur involving rearrangement of the $4f$ electrons—the incomplete shell. The atoms are thus put into the excited state. The lifetime of the excited state is a function of temperature since thermal agitation facilitates the return of electrons to their ground state, and this return is accompanied by an emission of light. This return, in the case of a given phosphorescence band, begins at a certain temperature and, at a certain higher temperature the thermal agitation causes the complete return thus setting temperature limits to the phosphorescence band. The return to the normal state may take place at a lower temperature if mechanical energy is applied sufficient to break the material with emission of TL.

Substances showing *Emission b* need no source of excitation of TL other than mechanical breaking. In addition to showing *Emission a* fluorite shows *Emission b* which may be observed by breaking the crystals after they have been heated to redness. The rare earth bands may be seen in this spectrum showing that the impurity atoms are taking part in the emission. Uranium nitrate in which mechanical breaking is the only source of excitation needed for TL also shows *Emission b* showing the characteristic bands of uranium in the spectrum. It appears probable that sphalerite, barium chloride and zinc sulphide also show *Emission b*.

Substances showing *Emission c* have an electric discharge in air when the crystals are broken giving the characteristic spectrum of nitrogen. This is the type of emission from pure substances and it appears to be due to distortions or breaking of the crystal lattice. Harvey's[5] work in which the character of the discharge is shown to depend upon the gas in which the crystal is broken indicates the source of this TL. He

[13] N. Riehl, Ann. d. Physik **29**, 640 (1937).
[14] J. Ewles, Trans. Faraday Soc. **35**, 119 (1939).
[15] Wick and Gleason, J. Opt. Soc. Am. **9**, 639 (1924).

suggests that, when the crystal is broken, positive and negative regions are developed and that discharges take place between such regions. It is evident that *Emission c* may also be present in crystals which show *Emission a* or *Emission b*.

Summary

(1) The effect of x-rays in exciting TL in certain materials is similar to that of radium.[1, 2] TL characterized as *Emission a* is excited by both of these agencies in luminescent materials in which there are activators such as the rare earths in fluorite or manganese in calcium sulphate. *Emission b* and *Emission c* are not excited by x-rays.

(2) TL, *Emission a*, is definitely related to other manifestations of luminescence. For each phosphorescence or thermoluminescence maximum there is a TL of the same color at a somewhat lower temperature.

(3) Changes in the temperature of exposure to x-rays produce marked differences in the TL resulting from exposure. In general, exposure at low temperature produces a greater effect than exposure at room temperature.

(4) Changes in the temperature of grinding produce marked difference in the intensity of emission. For substances showing *Emission a* there are definite temperatures of maxima of emission of TL. Substances like fluorite show a number of such maxima each related to a phosphorescence or thermoluminescence maximum of the same color which occur at a somewhat higher temperature. In a number of substances showing *Emission b* and *Emission c* which are not excited to TL by exposure to x-rays the effect of temperature of grinding is very marked. The lower the temperature of grinding the more intense the TL.

(5) Excitation of TL in substances showing *Emission a* appears to be due to some agency which causes a displacement of electrons in certain energy levels of the activator atoms. The return of the electrons to normal condition is accompanied by an emission of light. This takes place at a certain temperature giving phosphorescence or fluorescence but when mechanical energy is supplied the return takes place at a lower temperature with the emission of TL. *Emission c* appears to be an electric discharge which takes place when a crystal is broken. *Emission b* may possibly be a secondary effect which takes place when the electric discharge, *Emission c*, excites the crystal which is broken to luminescence, no further source of excitation being needed. This may account for the TL of such substances as uranium nitrate.

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Haidinger's Rings in Curved Plates

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The paper describes and illustrates the Haidinger interference patterns observed in curved plates of uniform thickness but of arbitrary form, and discusses their theory. Using an illuminated screen as light source and a limited viewing aperture, it is possible to observe such patterns with curved plates, their configuration depending upon the form of the plate as well as the position of the aperture with reference to the centers of curvature of the surface of the plate. It is pointed out that the interference pattern for a curved plate is geometrically similar in form to the image of the standard Haidinger pattern of circular rings as seen viewed by reflection at the appropriate distance from the curved surface of the shell.

1. INTRODUCTION

THE "interference curves of equal inclination" in transparent plates first observed by Haidinger are of great importance in physical optics. For their practical application in the field of spectroscopy, the plane-parallelism of the plate exhibiting these interferences is so essential that great stress is naturally laid on this requirement, and the tendency has therefore been to regard such plane-parallelism as a *sine-qua-non* for the observation of Haidinger's phenomenon. Actually, however, this is far from being the case, and by suitable arrangements the interference curves of equal inclination may be observed in a variety of other circumstances. In particular, these figures are readily to be seen in the transmission or reflection of light at the surface of curved transparent shells of uniform thickness but of arbitrary shape. They then assume a variety of forms depending on the circumstances of observation. From the standpoint of general optics, this enlarged field for the study of Haidinger's phenomenon is not without interest, and it is proposed in this communication to place on record some remarks and observations dealing with it.

2. METHODS OF OBSERVATION

To observe or photograph the Haidinger rings by reflection, a convenient arrangement is to use an opaque diffusing screen which contains a small aperture at its center. This is placed behind the plate under observation and is illuminated on its front by the light of a mercury lamp, while the eye or the camera is directed from the rear through the aperture and the plate towards a dark background. The arrangement permits of the observing aperture being brought very close to the plate, which is of great advantage if the latter is uniform over only restricted areas on its surface. For instance, interferences exhibiting hundreds of concentric rings may easily be observed with this arrangement in suitable areas on any ordinary glass plate such as a cleaned photographic negative. The advantage of restricting the aperture of observation and of bringing it close to the surface is equally evident in the observation of the transmitted system of rings. For the latter purpose, all that is necessary is to view an illuminated screen through the plate held close to the eye. As the plate is moved about, the complete system of rings suddenly springs into view when areas of sufficiently uniform thickness come in front of the eye, while with other parts of the plate nothing is to be seen on the viewing screen.

It is worthy of remark that the Haidinger interferences in a transparent plate may also be exhibited, either in reflection or in transmission, using a point source of light. For this purpose, we merely reverse the roles played by the aperture and the diffusing screen in the arrangements described above. A small aperture in an opaque screen closely backed by a mercury lamp is the origin of a divergent pencil of monochromatic light in the path of which the transparent plate is held. The reflected system of rings is then formed on the rear surface of the screen containing the illuminating aperture. The transmitted system of rings may similarly be observed when the diverging beam after passage through the plate falls on a viewing screen. Though these

arrangements are in certain respects less satisfactory than those in which an extended light source is employed, they are nevertheless of interest as showing that such a source is not indispensible for the observation of Haidinger's rings. In what follows, however, it is to be understood that we are referring to the method of observation first described above, unless otherwise explicitly stated.

3. Some Geometrical Considerations

Using an extended light source and a limited aperture of observation, the interference lines of equal inclination may readily be demonstrated with curved plates of any shape. If such plate be of uniform thickness, it is not necessary that the observer's eye should be placed close to its surface. Indeed, a special point of interest in the case is that the configuration of the interference curves varies with the position of the observer's eye. With the eye sufficiently close to the plate, the rings have the same form as for a plane-parallel plate. As the eye recedes from the plate, the curvature of the surface modifies the inclination of the normals to the reflected or transmitted rays which reach the eye; when the eye is sufficiently remote from the plate, its curvature determines such inclinations almost exclusively. The interference curves of equal inclination therefore progressively alter in form and finally reach a limiting configuration which is determined by the shape of the curved shell and which would, in general, be quite different from the familiar arrangement of concentric circular rings.

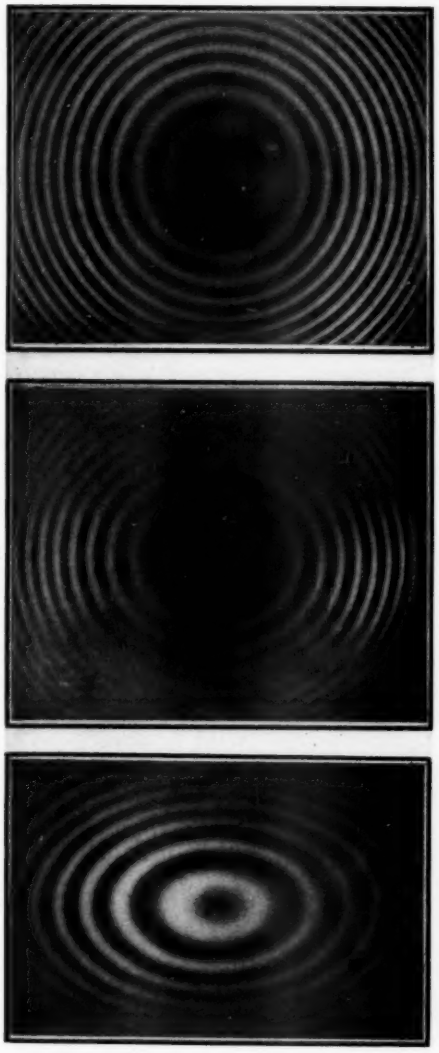
A closer consideration of the geometric problem which here arises indicates that the configuration of the interferences would depend greatly on whether the principal curvatures of the plate are turned towards the observer or away from him, as also upon the situation of the eye with respect to the centers of such curvature. To appreciate the reason for this, we may consider the case of a curved shell in the form of a spherical bowl with its concavity towards the observer. When the eye is exactly at the center of the bowl, all the rays reaching it will be normal to the surface, while if it be situated either nearer or further from the shell, the inclinations of the rays to the normals would increase from the vertex outwards. For this position of the eye, therefore, the circles on the sphere representing varying inclinations of the normal to the light rays would be very widely spaced and they would also shift rapidly as the eye is moved. For the same reason, in a case in which only one of the principal curvatures of the shell faces the observer, both the form and the spacing of the curves of equal inclination would alter rapidly with the position of the eye when the latter is near the center of curvature. On the other hand, if both the principal curvatures are turned away from the observer, no such singularity would be noticed, but the configuration of the interference curves would alter continuously as the eye recedes from the surface of the shell. In general, the form of the interference curves would depart the more widely from circular symmetry the greater the difference is between the principal curvatures at the vertex of the shell opposite to the observer.

4. Observations with Curved Plates

The theoretical considerations set out above are readily capable of experimental test. That a plane-parallel plate is not necessary for the observation of Haidinger's rings may be readily demonstrated with a spherical bulb of glass blown rather thin but uniform and examined by the method already described. The material most suitable, however, for a detailed study of the interference phenomena of curved plates is mica, which was indeed the substance with which Haidinger discovered his rings.[1] Mica is readily bent and held in a cylindrical form, and the various points discussed above may readily be examined with it. When such a cylinder is held with its convexity towards the observer and its axis horizontal and is gradually moved away from the eye, the Haidinger curves progressively change in form from a set of concentric circular rings, to concentric elliptic rings with the major axes horizontal and finally to a set of straight lines parallel to the generating lines of the cylinder.

The accompanying reproductions illustrate the foregoing remarks. Fig. 1 is a picture of the Haidinger's rings in a plane sheet of mica. Fig. 2 is a picture of the rings in a convex cylindrical sheet held fairly near the lens of the camera.

[1] See also Rayleigh, Phil. Mag. **12**, 489 (1906) and Chinmayandandam, Proc. Roy. Soc. **A95**, 176 (1918).



FIGS. 1, 2 AND 3. Haidinger's rings: (1) in a plane sheet of mica; (2) in a convex cylindrical sheet of mica held near the camera lens; (3) same as (2), but with sheet farther from camera lens.

Fig. 3 is a picture taken with the sheet moved further away from the lens, and it will be seen by comparison with Fig. 2 that the ellipticity of the rings is thereby increased. All the three photographs are of the reflected system of rings taken by the method described earlier in this communication.

When the cylinder of mica has its concavity towards the observer, the axis being horizontal, the sequence of changes with increasing distance of the eye from the mica is quite different. We have at first concentric circular rings which change to concentric elliptical rings with the *major axes vertical*, and after passage of the eye through the center of curvature, to circular rings once again, then to elliptical rings with the *major axes horizontal* and finally to straight lines parallel to the generating lines of the cylinder. In the passage through the center of curvature, the configuration of the rings is very varied and depends on the exact form of the mica. When this has the shape of a hyperbolic cylinder, the pattern is observed to consist of two sets of rings joined by oval curves similar to the well-known figures exhibited by a biaxial crystal in the polarization microscope.

5. Relation to Geometry of Image Formation

It has already been mentioned that the Haidinger pattern of a plate may be observed with a point source of light and a viewing screen to receive the light transmitted or reflected by the plate. A remarkable fact observed with curved plates in this connection is that *the transmitted and reflected systems of rings behave in a wholly different manner*. The transmitted ring-system seen in this way alters in form with the shape of the plate and its distance from the light-source in the same manner as in the usual method of observation. On the other hand, the reflected interferences remain of invariable form as a system of concentric circular rings, whatever may be the shape of the plate or its position. In both cases, however, the linear dimensions of the pattern seen on the screen increase with its distance from the source of light. The explanation of these facts becomes clear when we trace the formation of the interference curves, by following the rays delineating them from the source to the screen. The curves of equal inclination as traced on the surface of the plate would be of identical form in the two cases. In the case of the reflected system, however, the approach of the curve of a particular order of interference towards the vertex of the shell produced by the curvature of the latter is exactly set off by the recession from the vertex produced by the same curvature in the act of reflection of the ray before it reaches the

screen. The effect of the curvature of the shell on the reflected system is thus to alter the distribution of intensity of light on the screen without producing any change in the form or position of the interferences. On the other hand, in the transmitted system, the interference curves seen on the screen are the direct projections of the curves as traced on the surface of the plate and hence exhibit forms depending on the shape of the plate and its distance from the source.

The foregoing considerations indicate that the Haidinger pattern of a curved plate may be regarded as the geometric image of a pattern of the standard type consisting of concentric circular rings as seen by reflection at the curved surface of the plate. The facts as already described then become easier to grasp in the light of the well-known theory of image formation in geometrical optics. That this idea can form the basis for an exact theory of the Haidinger patterns of curved plates can be shown in the following way. A small white circular disk with a central aperture in it is illuminated by monochromatic light and held close to the eye. It is then viewed through the same aperture by reflection at the surface of a curved plate of mica. It is then observed that the configuration of the circular edge of the disk runs exactly parallel to the course of the interference rings seen projected on its surface. Indeed, the changes in the form of the reflected image of the disk in the most varied circumstances describe also the changes in the configuration of the interference rings, thus establishing the thesis stated.

6. Position of Best Focus

An interesting question which is closely related to the topic discussed above relates to the position in space where the Haidinger pattern of a curved plate is seen most clearly in focus. As the visibility of the pattern essentially depends on the limitation of the aperture of observation, and as this aperture is necessarily finite, a certain lack of definition is inevitable. This may however be minimized by suitable accomodation of the observer's eye or focusing of the camera employed to photograph the pattern. The focus would evidently be best when the angle between the normals and the corresponding rays reaching a given point in the image vary as little as possible. When the curvature is small or when the aperture is close to the shell, we should therefore focus for infinity in the same way as for a plane-parallel plate. For greater curvatures of the shell or with increasing distance of the aperture from it, the variation of the angle referred to over the surface of the shell becomes more rapid. We may reduce this variation by altering the focus so as to approach the surface of the shell, but this on the other hand would introduce a variation of the inclination of the rays from the same area of the shell which come to a focus at an image point. The best focus is determined by these opposing considerations which indicate that as the form of the interference curves alters progressively from the standard configuration of concentric circular rings to one determined completely by the form and curvature of the shell itself, the focus of the pattern also shifts steadily from infinity towards the surface of the shell. This general statement must, however, be qualified in certain respects. If the principal curvatures of the shell differ greatly in magnitude or in sign or in both, it is clear that the focusing would show a certain astigmatism, features in the pattern running in one direction being more clearly seen than features running in a perpendicular direction. It is also to be remarked that the focusing of the pattern as a whole would be difficult when the observing aperture is placed at or near a center of curvature of the surface.

From what has already been stated, it is evident that the interference curves of equal inclination for a strongly curved shell at oblique incidences would be best seen when the eye is focused on the surface of the shell itself. A limitation in the area of the light source employed to the extent of practically restricting it to a line-source running parallel to the interferences should then be of marked advantage. For, such a restriction would result in the angle of incidence of the light being better defined and therefore in a better definition of the fringes, since these depend for their visibility on the variation of the angle of incidence over the surface of the shell. In these respects there is a certain similarity with the behavior of the interference curves in plates of varying thickness, though the behavior in other respects is wholly different.

The Optical Properties of Semi-Transparent Sputtered Films Determined by Interference of Light

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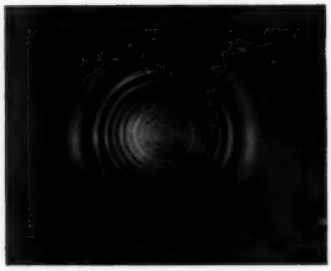
A study has been made of the optical properties of semi-transparent films of variable thickness produced by sputtering in hydrogen. The masses of the films have been computed from the assumed optical constants and densities of the metals, and from the locations of the interference fringes, when the films are viewed by reflected monochromatic light at approximately normal incidence. With few exceptions the computed masses are much greater than the masses determined directly by weighing. The differences between the computed and weighed masses can be accounted for by assuming higher refractive indices and lower densities of the films than those assumed for the bulk metals. Such would be the case if the films were composed of compounds, e.g., oxides of the metals. This has been verified by a colorimetric analysis of the iron films. Further confirmation is supplied by a study of the optical dispersion of the films, which seems to be characteristic of transparent insulators rather than of the metals. High refractive indices are also called for from a consideration of the aging of a platinum film. A mathematical analysis of the reflectivity of the films has been made, based upon the consideration of mutiple reflections within the films. To account for the number of fringes observed, very low indices of absorption must be assumed, such as possessed by transparent insulators.

THE optical properties of thin films have been the subjects of many investigations extending over a long period of years. It has been the aim of investigators to study the refractivity, transmission, and absorption of the film as functions of its thickness; to measure phase changes at the surfaces; and reflectivity of the film with its generally transparent backing medium. Broadly speaking, the methods of investigation that have been employed may be divided into three general classes, or combinations of these, namely, (a) the polarimetric; (b) the light intensity; and (c) the interference method.

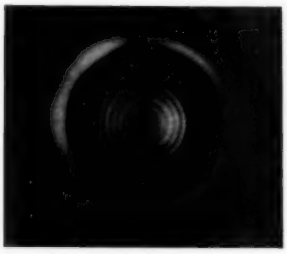
The polarimetric method of studying films upon metals was initiated by Drude,[1] and has been recently applied to practical problems by Tronstad,[2] and Leberknight and Lustman.[3] Försterling[4] and Essers-Rheindorf[5] have shown how the optical constants and thickness of a film mounted on glass might be obtained from the state of polarization of the reflected and transmitted light.

It is possible to evaluate the optical constants of the film from measurements of the intensities of the reflected and transmitted beams, combined with a knowledge of either the mass or thickness of the film. The reflectivity may be measured with either the film or glass mounting facing the incident beam. The more recent examples of this type of analysis are afforded by the work of Goldschmidt and Dember,[6] Schuch,[7] Murmann,[8] Goos,[9] Wolter,[10] and Koller.[11] Extensive researches have been carried out by Rouard[12] on the phase changes of light occurring at the bounding faces of films. Edwards[13] and Bauer[14] have also studied these phase changes and the interference of light in metallic films. The optical properties of alkali metal films in the ultraviolet region have been investigated by Wood[15] by means of polarization and transmission measurements, and the thickness evaluated from the interference bands in the films. The study of Newton's rings in sputtered films of variable thickness has been

[1] P. Drude, Wied. Ann. **36**, 532 (1889); **39**, 481 (1890).
[2] L. Tronstad, Trans. Faraday Soc. **29**, 502 (1933); **30**, 349 (1934).
[3] C. E. Leberknight and B. Lustman, J. Opt. Soc. Am. **29**, 59 (1939).
[4] K. Försterling, Göttingen Nachrichten, p. 58 (1911); Ann. d. Physik **30**, 745 (1937).
[5] G. Essers-Rheindorf, Ann. d. Physik **28**, 297 (1937).
[6] H. Goldschmidt and H. Dember, Zeits. f. tech. Physik **7**, 137 (1926).
[7] E. Schuch, Ann. d. Physik **13**, 297 (1932).
[8] H. Murmann, Zeits. f. Physik **80**, 161 (1933).
[9] F. Goos, Zeits. f. Physik **100**, 95 (1936); **106**, 606 (1937).
[10] H. Wolter, Zeits. f. Physik **105**, 269 (1937).
[11] K. Koller, Zeits. f. Physik **110**, 661 (1938).
[12] P. Rouard, Ann. de physique **7**, 291 (1937); Comptes rendus **206**, 1106 (1938); **208**, 1146 (1939).
[13] H. W. Edwards, Phys. Rev. **38**, 166 (1931).
[14] J. Bauer, Ann. d. Physik **20**, 481 (1934).
[15] R. W. Wood, Phys. Rev. **44**, 353 (1933).



(a)



(b)

FIGS. 1a AND 1b. Interference fringes in a circular film sputtered from an iron cathode in (a) hydrogen, and (b) oxygen.

carried out by Prosad and Sharan,[16] Prosad and Ghosh,[17] and Nathanson.[18]

Some time ago, a report was made by one of the authors[18] upon the interference of light in films formed by cathode sputtering in hydrogen. In the production of these films, the exposed surface of the cathode was made purposely small and placed relatively close to a Pyrex glass plate, upon which the deposit was made. The metals used as cathodes were manganese and platinum. The films produced were of variable thickness. If circular in shape, the films were either of the "mound" or "volcano" form; or if rectangular in shape, they were of the "plateau" form, one side of which sloped down to zero thickness. When examined by monochromatic light reflected at about normal incidence, the films revealed a series of interference fringes whose outlines depended upon the shape of the film. This is illustrated by the photographs of Fig. 1a and 1b, which show the fringes in a "mound-shaped" film produced from an iron cathode, when the residual gas is hydrogen and oxygen, respectively. The fringes were observed by light of wave-length 5461A. Employing these fringes as contour lines, the masses of the films were computed on the assumption that the density and optical constants were the same as for the metal in the bulk. It was found that the masses of the manganese films checked quite reasonably with masses as obtained by weighing, but that the computed masses of the platinum films were about two and one-half times as large as the weighed masses.

Since then, the study of these films has been extended to other metals, and this article constitutes a further report on the characteristics of the films thus produced. It has been found that there is quite a variation in the ease with which this type of film can be formed from the various metals serving as cathodes. Sputtered films exhibiting these interference fringes are most easily formed from manganese, tin, and iron cathodes. Next in order of ease of production is platinum, while films from copper and nickel cathodes are produced with much greater difficulty. Sputtering with silver and gold cathodes failed to produce films exhibiting these interference fringes, no matter how the pressure of the residual hydrogen or the current and discharge voltage were varied. Films which do exhibit these fringes are semi-transparent and straw-colored by transmitted light.

The discharge chamber[19] employed was of the customary bell jar type as shown in Fig. 2. All of the metallic parts are encased in either Pyrex glass or mica, *M*, except for an opening beneath the cathode, *C*. By means of the ground glass joints, *BD*, a pair of mica butterfly wings, *SS*, fastened to the tops of the glass rods, *R*, could be interposed between the cathode and Pyrex glass plate, *P*, in order to shield the latter from any deposit during an initial period of sputtering lasting about one-half hour, the purpose of which was to cleanse the cathode surface. The glass plate rests upon the glass table, *T*. The hydrogen was produced electrolytically and dried by

[16] K. Prosad and S. Sharan, Ind. J. Phys. **8**, 425 (1934).
[17] K. Prosad and B. N. Ghosh, Ind. J. Phys. **10**, 49 (1936).
[18] J. B. Nathanson, J. Opt. Soc. Am. **23**, 388 (1933).

[19] A very extensive bibliography on cathode sputtering, covering the period from 1852 through 1931, is given by H. F. Fruth, Physics **2**, 280 (1932). More recent discussions of this subject are given by J. A. Darbyshire, J. Sci. Inst. **10**, 83 (1933); E. O. Hulburt, Rev. Sci. Inst. **5**, 85 (1933); E. N. Da C. Andrade and J. G. Martindale, Phil. Trans. London **A235**, 69 (1935); and P. Rouard, Ann. de physique **7**, 291 (1937).

passing through a train of tubes containing calcium chloride and phosphorus pentoxide. A small neon sign transformer served as a source of high voltage for the electrical discharge, rectification being accomplished by means of a small anode, A, of tungsten wire, situated outside the main discharge chamber.

The voltage during sputtering depended upon the gas pressure, the current, and the nature of the cathode, the range of values extending from 2300 to 3500 volts. The discharge current was as low as a fraction of a milliampere for metals such as silver, and as high as 10 milliamperes for the slower sputtering metals. The gas pressure varied from 0.15 to 4 mm of mercury, the discharge conditions being so adjusted that the edge of the Crookes dark space was almost but not quite in contact with the surface of the Pyrex glass plate upon which the film was deposited.

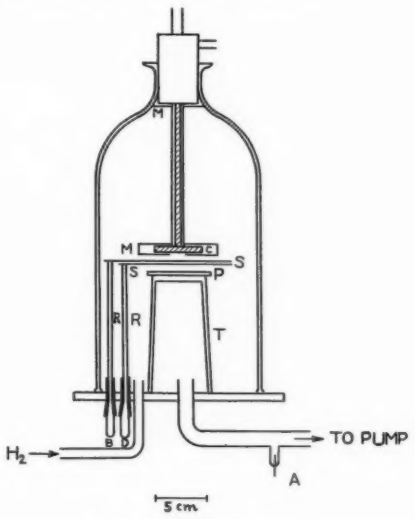


FIG. 2. Sputtering chamber.

The volumes of the films were computed by regarding them as being built up out of a large number of very thin disks of variable areas, placed one on top of another. The thickness of that part of the film corresponding to two adjacent fringes was taken as one-half a wavelength in the film. The thickness of the film at the outermost or first dark fringe (as one proceeds from zero to increasing thickness) was computed on the basis of the electromagnetic theory as outlined in a previous paper.[18] The fringes were assumed to be produced by the interference of the two reflected rays, E_1 and E_2 (Fig. 3), ray E_1 being reflected directly from the air-film surface and ray E_2 from the film-glass surface. The phase changes were computed for all the reflections and refractions involved, and it was assumed that the first dark fringe occurs for a thickness of film such that rays E_1 and E_2 differ in phase by 180°.

A summary of all of the results for a wavelength of 5890A is given in Table I,[20] where n is the refractive index and k the index of absorption. The optical constants of the metals were obtained from the *International Critical Tables*.[21] Where possible (e.g., nickel and iron) those optical constants were chosen which were given for metallic mirrors formed by sputtering.[22]

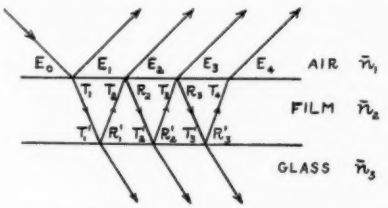


FIG. 3. Multiple reflections within a film.

In general, the agreement between the computed and weighed masses is rather poor. An inspection of Table I shows that the best agreement is obtained with manganese, and that the disagreement is the greatest for copper. It is significant that in the last-named case, the refractive index of the metal is the lowest. Better agreement calls for higher refractive indices than are afforded by the values generally given for these metals. It is true that abnormally high refractive indices have been found[23] for films whose thickness is less than a certain critical value varying from 2 mμ to 26 mμ. Kindinger and Koller[24] have recently pointed out that discrepancies in the values of the optical constants

[20] We are indebted to H. S. Seifert for observations on copper; to R. E. Warren for some of the observations on tin; and to H. Oshry, on nickel.

[21] Int. Crit. Tab., Vol. 5.

[22] W. Meier, Ann. d. Physik **31**, 1017 (1910).

[23] B. Pogany, Ann. d. Physik **49**, 531 (1916); J. Richter, Ann. d. Physik **77**, 81 (1925); R. Schulze, Physik. Zeits. **34**, 24 (1933).

[24] M. Kindinger and K. Koller, Zeits. f. Physik **110**, 238 (1938).

of films of thicknesses ranging from 5 to 30 mμ are to be ascribed to a large gas absorption. In our investigation, however, most of the film possessed a thickness quite in excess of these critical thicknesses.

Lamellar Reflectivity for Multiple Reflections

The discrepancies between the weighed and computed masses of the films indicate that an incorrect choice has been made for either the optical constants or the densities, or both. It was thought that considerable information regarding the optical constants might be obtained from a theoretical calculation of the reflectivity of the film and glass; i.e., the lamellar reflectivity for normal incidence as a function of the thickness of the film, since for the proper values of n and k such an expression should exhibit maxima and minima corresponding to the observed interference fringes. Furthermore, in the derivation it was thought desirable to take into account an infinite number of internal reflections within the film.

The amplitudes of the electric vectors of the various rays will be indicated as shown in Fig. 3, where for convenience of labeling, the rays are not shown as incident normally on the faces of the film. Unprimed letters refer to the air-film surface; primed letters refer to the film-glass interface. The application of the usual boundary conditions to any face leads to the following Fresnel reflection and transmission coefficients, such as r_{12}, t_{12}, etc., where the subscripts refer to the media as indicated, and in the order of the passage of the light ray.

$$\left.\begin{aligned} &r_{12}=(\bar{n}_1-\bar{n}_2)/(\bar{n}_1+\bar{n}_2), \quad t_{12}=2\bar{n}_1/(\bar{n}_1+\bar{n}_2),\\ &r_{23}=(\bar{n}_2-\bar{n}_3)/(\bar{n}_2+\bar{n}_3), \quad t_{21}=2\bar{n}_2/(\bar{n}_1+\bar{n}_2),\\ &r_{12}=-r_{21}. \end{aligned}\right\} \quad (1)$$

The bars over the refractive indices indicate complex quantities defined by $\bar{n}=n(1-ik)$, where k (the optical index of absorption) is given by $E=E_0\exp(-2\pi nkz/\lambda_0)$, λ_0 being the wavelength in vacuum, and z the distance traversed by the ray. Hence $E_1=r_{12}E_0$; $T_1=t_{12}E_0$; $R_1'=r_{23}T_1'$; $R_2=r_{21}T_2$, etc., where $T_1'=T_1\exp(-i2\pi\bar{n}_2z/\lambda_0)$ $=T_1Z$, and Z is used as an abbreviation for the exponential term.

Making use of these relations, it follows that two successively reflected amplitudes such as E_3 and E_2 are connected by the following relation:

$$E_3=QE_2, \quad \text{where} \quad Q=r_{23}r_{21}Z^2. \quad (2)$$

The resultant reflected amplitude E_r is given by

$$\begin{aligned} E_r&=E_1+E_2+E_3+\cdots\\ &=E_1+E_2(1+Q+Q^2+Q^3+\cdots)\\ &=E_1+E_2/(1-Q), \end{aligned}$$

since $|Q|<1$ and the series is infinite. Again making use of the relations between the amplitudes and the various reflection and transmission coefficients, it follows that $E_2=t_{12}t_{21}r_{23}Z^2E_0$, and hence

$$E_r=-\left(\frac{E_0}{1-r_{21}r_{23}Z^2}\right)[r_{21}-Z^2r_{23}(t_{12}t_{21}+r_{21}^2)]. \quad (3)$$

Table I. *Films sputtered in hydrogen.*

Film No.	Nature of Cathode	Shape of Film	n	k	Density g/cm³	Masses in mg		Ratio
						Computed A	Weighed B	A/B
1	Tin	Rect.	1.13	4.08	7.29	9.94	6.02	1.65
2	Tin	Circ.	"	"	"	3.41	1.98	1.72
3	Tin	Rect.	"	"	"	15.90	10.50	1.51
4	Iron	Circ.	1.51	1.08	7.90	2.57	1.07	2.40
5	Iron	Circ.	"	"	"	7.57	2.57	2.94
6	Manganese	Circ.	2.26	1.64	7.44	3.40	3.97	0.86
7	Manganese	Circ.	"	"	"	2.70	2.67	1.01
8	Platinum	Rect.	2.01	2.10	21.45	11.46	4.09	2.80
9	Platinum	Circ.	"	"	"	6.35	2.55	2.49
10	Nickel	Circ.	1.30	1.52	8.7	2.29	1.58	1.45
11	Nickel	Circ.	"	"	"	1.64	1.57	1.04
12	Copper	Circ.	0.63	4.09	8.9	7.95	1.90	4.18
13	Copper	Circ.	"	"	"	9.11	1.86	4.89
14	Copper	Rect.	"	"	"	26.2	4.14	6.33
15	Copper	Rect.	"	"	"	75.2	10.3	7.30

But from a consideration of the Fresnel coefficients, $t_{12}t_{21}+r_{21}^2=1$. Hence finally

$$E_r=-E_0(r_{21}-r_{23}Z^2)/(1-r_{21}r_{23}Z^2). \quad (4)$$

The lamellar reflectivity R is obtained by evaluating the absolute value of the square of E_r/E_0. Letting the first medium be air for which $\bar{n}_1=1$; the second medium, the film for which $\bar{n}_2=n(1-ik)$; and the third medium, Pyrex glass for which $\bar{n}_3=N$, the final result is given by (5):

$$R=\frac{A^2+B^2-2e^{-k\theta}[(Aa+Bb)\cos\theta-(Ab-Ba)\sin\theta]+(a^2+b^2)e^{-2k\theta}}{C^2+D^2-2e^{-k\theta}[(Cc+Dd)\cos\theta-(Cd-Dc)\sin\theta]+(c^2+d^2)e^{-2k\theta}} \quad (5)$$

where

$$\begin{aligned} A&=(n-1)(n+N)-n^2k^2, & B&=nk(2n+N-1),\\ a&=(n+1)(n-N)-n^2k^2, & b&=nk(2n-N+1),\\ C&=(n+1)(n+N)-n^2k^2, & D&=nk(2n+N+1),\\ c&=(n-1)(n-N)-n^2k^2, & d&=nk(2n-N-1),\\ \theta&=4\pi nz/\lambda_0. \end{aligned}$$

Equation (5) is a very interesting formula which contains all of the fluctuations in the intensity of the reflected light arising from interference, either in an absorbing or nonabsorbing film. For example, in the case of a nonabsorbing layer with air on both sides, $N=1$ and $k=0$, Eq. (5) reduces to the well-known expression[25] for the reflectivity of a glass plate, namely,

$$R=\frac{4r^2\sin^2\theta/2}{1+r^4-2r^2\cos\theta}, \quad (6)$$

where $r=(n-1)/(n+1)$.

Equation (5) also yields the proper conditions for zero reflectivity of a nonabsorbing film on glass. In this case it reduces to

$$R=(r^2-2rr'\cos\theta+r'^2)/(1-2rr'\cos\theta+r^2r'^2) \quad (7)$$

where r is as given previously, and $r'=(n-N)/(n+N)$, the Fresnel reflection coefficient of the film-glass interface. The numerator of (7) has a simple geometric interpretation, being merely the square of one side of a triangle whose other two sides are r and r', with θ as the included angle. There are only two ways in which R can be zero; namely, $\theta=0$, and $r=r'$; or $\theta=\pi$, with $r=-r'$. The first leads to the result, $N=1$, which is the case of a transparent film in air, whose thickness $z=I\lambda_0/2n$ where I is zero or any integer. The second and more interesting condition for zero reflectivity leads to $(n-1)/(n+1)=(N-n)/(N+n)$ or $n^2=N$, with $N>n$, and the thickness given by $z=(2I+1)\lambda_0/4n=(2I+1)\lambda_m/4$ where λ_m is the wave-length in the film. The last result is of course the physical basis of recent methods[26] that have been developed for rendering glass "invisible."

In Figs. 4, 5 and 6 have been plotted values of the reflectivity R for several combinations of n and k as a function of the thickness of the film expressed in units of λ_m. The optical constants chosen for the plotting of the graphs of Fig. 6 are typical of a metal such as tin or iron. The reflectivity increases with the thickness, passes through a slight maximum, and ultimately attains for thicknesses in excess of about $\frac{1}{2}\lambda_m$ a constant value characteristic of the metals in the bulk. The reflectivity for normal incidence is then given by the well-known expression $[n^2(1+k^2)-2n+1]/[n^2(1+k^2)+2n+1]$, which expression follows from (5) by neglecting the exponential factors and carrying out the proper algebraic reductions. For $k=0$, the graphs of Figs. 4 and 5 are those of sinusoidal curves and illustrate the formation of a series of interference fringes produced by a transparent film of variable thickness, adjacent fringes being located at points in the film differing in thickness by $\lambda_m/2$.

The general expression for the reflectivity of an absorbing film, given by Eq. (5), can be thrown into a more convenient form for interpretation, by means of the following substitutions:

$$\begin{aligned} \text{Let } A&=F\cos H, & a&=f\cos H,\\ B&=F\sin H, & b&=f\sin h,\\ C&=G\cos J, & c&=g\cos j,\\ D&=G\sin J, & d&=g\sin j,\\ \delta&=h-H, & \epsilon&=j-J. \end{aligned}$$

[25] See for instance p. 142 of *A Treatise on Light* by R. A. Houston.

[26] John Strong, J. Opt. Soc. Am. **26**, 73 (1936); Katherine B. Blodgett, Phys. Rev. **55**, 391 (1939); C. H. Cartwright and A. F. Turner, Phys. Rev. **55**, 595 (1939).

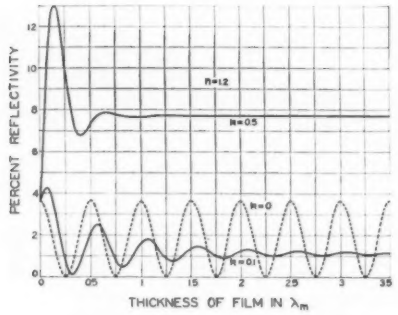


FIG. 4. Lamellar reflectivity of a film ($n=1.2$) on Pyrex glass.

Then (5) assumes the form

$$R=\frac{F^2-2Ffe^{-k\theta}\cos(\theta+\delta)+f^2e^{-2k\theta}}{G^2-2Gge^{-k\theta}\cos(\theta+\epsilon)+g^2e^{-2k\theta}}. \quad (8)$$

An inspection of Eq. (8) shows that both numerator and denominator represent the squares of the vector sums of two components, one of which, F, is independent of the thickness of the film, while the other, $fe^{-k\theta}$, is an exponentially damped vector whose value does depend upon the thickness of the film. The angles between the vectors in the numerator and denominator are the supplements of $(\theta+\delta)$ and $(\theta+\epsilon)$, respectively. The numerator and denominator thus represent damped cosine functions of the thickness of the film. These cosine functions are of equal periods, but in general have different phases. Because of the characteristics of the logarithmic spiral, it is very interesting to point out that the maxima and minima of reflectivity do not lie exactly $\lambda_m/2$ distance apart, as for nonabsorbing films, but are, however, only very slightly displaced from this value unless the index of absorption of the film is very large.

For a nonabsorbing film the first reflection minimum occurs at a thickness of $\lambda_m/4$, if $n<N$ (Fig. 4), and $\lambda_m/2$ if $n>N$, (Fig. 5). For absorbing films, it seems to occur between these two values. Assuming that the films possess the optical properties characteristic of the metal cathodes, then for all metals reported in this article, the first minimum of reflection, on the assumption of multiple reflections, should probably lie between $\frac{1}{4}\lambda_m$ and $\frac{1}{2}\lambda_m$, where λ_m is the wave-length in the film. These values are much larger than predicted by the analysis of phase changes outlined previously,[18] so that the computed values of the masses in Table I would be somewhat larger than those listed.

From Fig. 4 and Fig. 6, it is evident that the fluctuations in the reflectivity fade out rapidly with increase in k and thickness of the film, so that for the values of k such as have been measured for metals in the bulk, the absorption of light in the film is so great that even the first

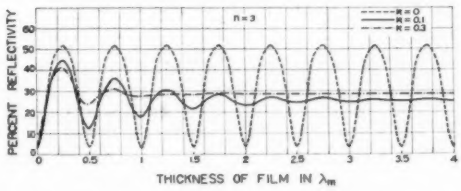


FIG. 5. Lamellar reflectivity of a film ($n=3$) on Pyrex glass.

minimum or dark fringe would be scarcely observable. This indicates that in all cases where distinct fringes are observed, the value of k must be considerably less than unity, with the maximum value not over 0.1. That many fringes were observed with sputtered films, especially those from metals such as platinum or iron, would indicate that these films do not possess the characteristics of the metals in the bulk, or else that the films are nonmetallic in character. As will be discussed, the last alternative seems to have been fairly definitely confirmed for iron.

SPUTTERED FILMS FROM AN IRON CATHODE

These films were produced by sputtering from a cathode of electrolytic iron, given as 99.97 percent pure. The iron, which was in the form of a thin plate about one inch square, was set into an aluminum block so that the face of the iron plate was flush with that of the aluminum. The whole was encased in mica, except for a circular opening $\frac{3}{4}$ inch in diameter, located as close as possible to the iron surface. During the formation of the films, the pressure of the residual hydrogen was maintained between 0.2 and 0.3 of a millimeter of mercury and the current between 1.3 and 2.1 milliamperes, while the discharge voltage was held in the range of 2500 to 3400 volts. No difficulty was experienced in obtaining films

revealing six to twelve fringes, the number depending upon the length of time of sputtering, which might be from 14 to 19 hours. The appearance of the films by transmitted light was of the orange-tinted type, quite similar to that of the films produced from other metals. The volume, and hence the masses of the films, were computed as previously outlined, assuming for the optical constants of iron[22] the values $n=1.51$ and $k=1.08$ for the wave-length $\lambda=5890$A. The computed and weighed masses are indicated in Table I.

The mathematical analysis based upon multiple reflections within the film indicates that for an absorption index as large as that used for iron, hardly any interference fringes should be visible. Since, however, six to twelve fringes were observable, the conclusion must therefore be drawn that the absorption index of the films could hardly have been greater than 0.1, and hence that the films produced under the experimental conditions outlined could hardly have been metallic. Iron oxidizes quite easily even under conditions where there is very little oxygen present, and hence it is plausible to assume that the films were composed of iron oxide. In order to test this assumption, the percent content of iron was determined as follows.

A colorimetric method of analysis was employed, based upon the conversion of the iron to ferric thiocyanate, $Fe(CNS)_3$. A set of standard solutions was made up containing known amounts of iron, previously dissolved in hydrochloric acid. The solutions were evaporated to dryness to remove the acid, and the residue dissolved in a known volume of distilled water. The same treatment was applied to the sputtered films. The standard and unknown solutions were then acidified with hydrochloric acid, to which were added a few drops of potassium permanganate, enough to oxidize all of the iron to the ferric condition. The presence of a faint pinkish color indicated that just enough permanganate had been added. Finally 10 cc of a solution containing about 50 g per liter of potassium thiocyanate were added, producing a red color, the intensity of which depended upon the iron concentration. All of the solutions were then diluted with distilled water to the same volume.

Samples of the various solutions were then successively introduced into a tubular glass cell, 15 cm long and 2 cm in diameter, the ends of which were closed by clear glass plates suitably cemented to the tube. The transmissions of the various standard and unknown solutions relative to distilled water were determined by means of a sensitive photoelectric cell circuit. The percent transmission was plotted *versus* the known percent iron concentrations, and the concentrations of the unknown solutions were obtained from this graph. In this manner it was found that the percent of iron in two different films was 74 and 67. On the assumption that the films consisted of a mixture of iron and ferric oxide, it follows from a simple computation that these films are 86.5 and practically 100 percent iron oxide, respectively. This virtually complete oxidation occurred during the sputtering process, since observations on the fringes were made both during and immediately after the sputtering. It may be quite likely that residual oxygen may have come over with the electrolytically produced hydrogen. At any rate, conditions for chemical reactions are quite favorable in an electrical discharge chamber.

Oxide Films

Assuming that the iron films are completely iron oxide, a recomputation was made of their masses. From an optical investigation of oxide films on steel and iron, Tronstad[27] has concluded that the refractive index of iron oxide for sodium light is about 3. This value is quite consistent with those given for hematite in standard tables. Assuming a density of 5.12 g/cm^3, the computed

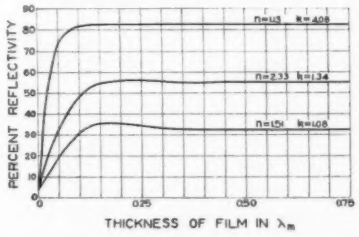


Fig. 6. Lamellar reflectivity of a film possessing optical constants characteristic of a metal.

[27] L. Tronstad. Kgl. Norske Videns. Selsk., Trondhjem. Skr. No. 1 (1931).

values of the films turn out to be 0.88 mg and 2.47 mg, as compared with the weighed masses of 1.07 and 2.57 mg, respectively. The agreement is thus reasonably satisfactory. It thus seems quite definitely established that under the present physical conditions of sputtering, these films will come down as iron oxide.

In order to test this point further, a film was produced from the iron cathode by sputtering in an atmosphere of oxygen. The conditions were thus most favorable for oxidation. The appearance of this film when viewed by monochromatic light is similar to that of the films produced in an atmosphere of hydrogen, as illustrated by the photographs of Fig. 1. The mass of this film (No. 16 of Table II) was computed using the constants of iron oxide, and was found to be 1.09 mg as compared with the weighed mass of 1.27 mg. The agreement is thus of the same order as that found for the films sputtered in hydrogen.

Prompted by the suggestion that the other films might also be in an oxidized condition,[28] a recomputation of the masses was made for some of the other films. Unfortunately, the densities, and especially the refractive indices are not known for all of the metals studied, so that the recomputation has been made only for some of the metals with the aid of tabular[29] data. The results of these computations are listed in Table II. The ratios of the computed to the weighed masses are much closer to the value of unity.

Optical Dispersion of the Films

The interference method of evaluating the masses of the films may be utilized to determine the variation of the refractive index with wave-length. This information may be obtained by reversing the order of computation; i.e., by solving for the refractive index from a knowledge of the weighed mass, density of the assumed oxide film, and the location of the interference fringes corresponding to several different wave-lengths. This is illustrated by examples taken from the data for tin, iron, and copper. The refractive indices are given in Table III. It is interesting to note that the dispersion comes out to be entirely different from that for the metals, and is analagous to that for a dielectric. While the refractive indices for these metals increase with increase in wave-length (copper possesses an irregular dispersion curve in the visible part of the spectrum), the opposite seems to be the case for these films. Attention has been called in a previous paper[18] to the similar behavior of manganese and platinum films. These results are in harmony with the observations by Kundt[30] upon the refractive indices of metal oxides in the form of small angle prisms. An examination of his data shows not only that the refractive indices of

[28] From a study of the chemical behavior of tin films sputtered in air or oxygen, Overbeck (J. Opt. Soc. Am. **23**, 113 (1933)) has concluded that the deposit must be in the form of stannic oxide. Recently L. H. Germer, Phys. Rev. **56**, 58 (1939), has studied the electron diffraction patterns of various metallic and nonmetallic films. These were deposited on Formvar foils by distillation in high vacuum. A freshly formed copper film of 138A mean thickness revealed the presence of cuprous oxide, which constituted 15 percent of the film. The percent oxide increased with decreasing thickness of the film so that films of thicknesses less than 14A were found to be completely oxide.

[29] Int. Crit. Tab., Vol. 1, 106 and 165; Landolt-Bornstein, Phys. Chem. Tab., 5th Ed., p. 734.

[30] A. Kundt, Wied. Ann. Phys. **34**, 484 (1888).

Table II. *Masses of oxide films.* $\lambda = 5890A$.

Film No.	Assumed Composition	n	Density g/cm³	Masses in mg: Computed *A*	Masses in mg: Weighed *B*	Ratio *A/B*
1	SnO_2	2.04	7.0	5.28	6.02	0.88
2	"	"	"	1.81	1.98	0.92
3	"	"	"	8.46	10.50	0.81
4	Fe_2O_3	3.0	5.12	0.84	1.07	0.79
5	"	"	"	2.47	2.57	0.96
12	CuO	2.63	6.4	1.37	1.90	0.72
13	"	"	"	1.57	1.86	0.84
14	"	"	"	4.52	4.14	1.09
15	"	"	"	12.9	10.3	1.25
16	Fe_2O_3	3.0	5.12	1.09	1.27	0.86

the oxides of iron, nickel, and copper are greater for blue light than for red light, but that these indices are greater than those for the corresponding metals, as demanded by the results of this investigation.

Aging of Platinum Films

The optical properties of the films obtained from a platinum cathode have been found to vary somewhat with age. A series of observations on the positions of the interference fringes was made on film No. 9 of Table I, extending over a period of about three and one-half years. When not under observation, the film was preserved in a desiccator. The diameters of the fringes as a function of the time in months are plotted in Fig. 7, observations having been made by sodium yellow light. The bottom curve corresponds to the thickest part of the film, the shift in fringe position being the least for the top curve, which corresponds to the thinnest part of the film. It was found that subsequent to the formation of the film, the fringe diameters tended to increase with age, assuming a constant value in about four to six months. The effect is more noticeable for the thicker portions of the film.

In attempting to determine the optical constants of the film, following the polarimetric method of Försterling,[4] it was necessary to place the film in contact with cedar oil. In the intervals between these polarimetric observations which extended over a period of several months, the oil was always carefully removed with the aid of ethyl alcohol, after which the film was dried and preserved in a desiccator. Subsequently upon measurement, the fringe diameters were found to have been reduced somewhat in size. However, with further aging, the ultimate diameters were regained. This process was repeated later, but over a much shorter period of time. The effect of contact with the liquids is shown in Fig. 7 by the dips in the curves for the ages of about 16 and 27 months.

To account for the phenomenon of the increase of fringe diameters with age, one is tempted at first sight to assume a thickening or "swelling" of the film, but on further consideration it can be shown that a diminution of the film thickness accompanied by a corresponding increase in the refractive index is sufficient to account for the phenomenon observed. Let us assume that a given fringe shifts in position whenever the optical path nz in the film is altered, where n and z are the refractive index and thickness at a given point of the film, respectively. Since the density ρ of the film might be assumed to vary inversely as the thickness, changes in the optical path would be proportional to changes in n/ρ. Considering the transparent character of the film, the relation between n and ρ might be assumed to be given by the Lorenz-Lorentz law, $(n^2-1)/(n^2+2)=C\rho$, where C is a constant of proportionality independent of n and ρ. The variation of the refractive index with the density is thus given by

$$dn/d\rho=(n^2-1)(n^2+2)/6n\rho. \qquad (9)$$

This equation indicates an increase of n with ρ, for all values of n greater than unity. Hence

$$d(n/\rho)/d\rho=(\tfrac{1}{6}\rho^2 n)[(n^2-1)(n^2+2)-6n^2]. \qquad (10)$$

Setting the last equation equal to zero, it appears that n/ρ will remain constant for $n=2.32$, but will increase with increasing density of a shrinking film, providing that the refractive index is greater than 2.32. Assuming a shrinking film thickness, circular fringes should therefore remain fixed in position with aging if the refractive index is just 2.32, but should either increase or decrease in diameter if the refractive index be greater or less than this critical value, respectively. In other words, due to an increase of n/ρ with density, a given fringe should shift to the thinner or outer portion of the film. Refractive indices greater than 2.32 may be expected from the previous discussions. Further evidence may also be drawn from the work of Kundt,[30] who found the refractive index of very thin prisms of a mixture

Table III. *Dispersion of films.*

	Refractive Index					
	Films			Metals		
λ in A	Tin No. 2	Iron No. 5	Copper No. 13	Tin	Iron	Copper
4359	2.12			0.713	1.27	
5461	1.97	2.96	2.33	0.940	1.42	1.01
5893	1.87	2.88	2.22	1.13	1.51	0.63
6708	1.68	2.74	2.02	1.43	1.71	0.67

of platinum and platinum oxide to be as high as 4.82 for white light.

From Eq. (10) it may be shown that the fractional change in the film density is related to the observed fractional change in the optical path by the expression,

$$\frac{\Delta\rho}{\rho} = \pm \frac{6n^2}{(n^2-1)(n^2+2)-6n^2} \frac{\Delta(n/\rho)}{n/\rho}, \quad (11)$$

where the plus sign is to be taken for a shrinking film and the minus sign for a "swelling" film. From the increase in fringe diameters with aging,

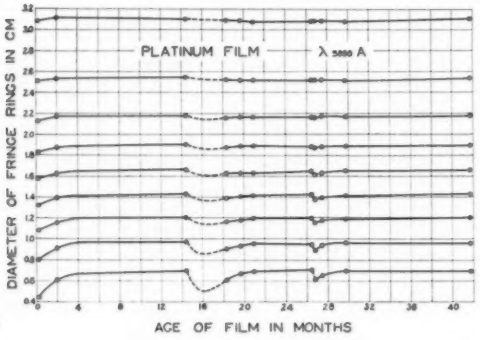


FIG. 7. Fringe diameters of a platinum film plotted as functions of aging.

it has been estimated that the increase in optical path of the platinum film was about 8 percent. The corresponding percent change in the density as given by Eq. (11) will depend upon the initial value of the refractive index. Hence for a small change in the density, say not to exceed 10 percent, the refractive index must be greater than 3.1 for a shrinking film, or less than 1.2 for a "swelling" film. Of the two alternatives, the former is the more probable, particularly as it calls for large refractive indices, in harmony with the previous evidence. A refractive index less than 1.2 for platinum or its oxides is contrary to optical observations.

For an initial refractive index of 4 for a shrinking film, an increase of 8 percent in the optical path will require only a 4.4 percent increase in the density or an equal decrease in the thickness. Such a change might be reasonably expected. Apparently the effect of the contact of liquids with the platinum film has been to produce a "swelling" of the film followed by a shrinking upon aging.

It is hoped to extend this investigation by studying the electrical conductivity of these films, as well as means for obtaining an independent measurement of the film thickness and the refractive index.

Influence of Pressure and Development on the Solarized Latent Photographic Image

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INTRODUCTION

ON account of the intangibility of the latent photographic image its nature can only be revealed by a study of its tangible manifestations. One of these manifestations or characteristics is the pressure effect.

This effect was first investigated by Warnercke[1] when he wrote on a photographic plate with a stylus using gentle pressure so as not to scratch the film. He found that, upon development, this writing developed out black. Volmer[2] repeated Warnercke's experiments and added that if the plate was fogged by daylight before development, then the marks came out white on a dark background. P. Wulff[3] investigated the effect of nonshearing and of shearing pressure before exposure and of shearing pressure after exposure in positive movie film. He found that pressure without shear caused a reduction in sensitivity, no latent fog being produced; while shearing pressure produced a latent fog.

F. E. Poindexter in his article entitled "A New Photographic Effect"[4] described the effect, on the latent image, of pressure applied during exposure. From his investigation he concluded that the application of pressure during exposure to light caused an appreciable reduction in the density of the latent image. Karl Maring, S. J., verified this statement in his dissertation,[5] displayed the density-log exposure curve for constant pressure and carried the exposure out to the beginning of the region of the second reversal.

More recently Ny Tsi-Ze[6] and his associates repeated the F. E. Poindexter pressure experiment and obtained identical results. In addition they varied the wave-length[7] of the light employed in the exposure and concluded that the pressure effect is greater for radiations in the red than in the violet end of the spectrum.

In the experimentation described hereafter, the influence of pressure and development (both chemical and physical) on the latent image will be noted. Special attention will be given to the phenomena in the region of reversal under the influence of these two agents.

APPARATUS

The apparatus employed in this experimentation is represented diagrammatically in Fig. 1. Pressure is applied, by means of a lever system, to the photographic material which is placed on top of the plate-glass block, *G*. The total length of the lever arm, i.e., the perpendicular distance from the axis, *P*, to the point of application of the weights, *W*, is 69.8 cm. The distance from *P* to the center of the pin *F* is 9.8 cm. *B*, the pressure ball, was obtained by grinding

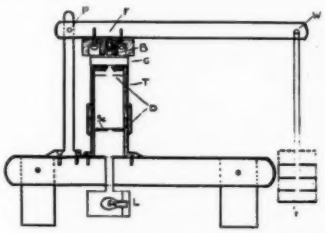

FIG. 1. Diagrammatical representation of pressure machine.

a flat surface on a steel ball bearing. This flattened pressure surface, which has a radius of 0.242 cm and a cross-sectional area of 0.184 cm², was polished to a mirror-like finish. The transmitted pressure of the weights at *W* causes the flattened side of the pressure ball to press down on the photographic material. To insure a uniform distribution of pressure at all times a ball bearing

[1] Warnercke, Phot. Archiv. 120 (1881).
[2] Volmer, *Phot. Umkelerungerscheinungen Treang. Diss.* (Leipzig, 1910).
[3] P. Wulff, Zeits. f. wiss. Phot. **23**, 145–48 (1925).
[4] F. E. Poindexter, J. Opt. Soc. Am. **21**, 59 (1931).
[5] Karl Maring, S. J., "The Influence of Pressure on the Formation of the Latent Photographic Image Particularly its Effect on Reversal in the Region of Solarization," St. Louis University Library.
[6] Ny Tsi-Ze and Chien Ling-Chao, Sci. et Indus. Phot., 2e serie, tome IV, 1–6 (1933); Comptes rendus **194**, 1644 (1932); Ny Tsi-Ze and Tsien Ling-Chao, Chinese J. of Physics **1, 2**, 66–76 (1934).
[7] Ny Tsi-Ze and Chien Ling-Chao, Comptes rendus **196**, 107 (1933).

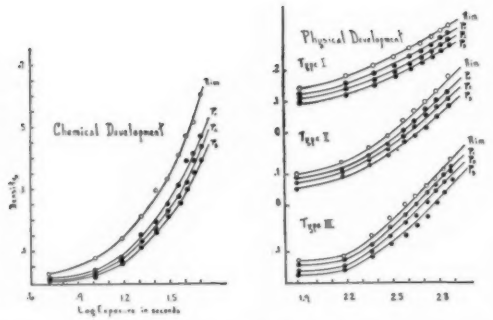

FIG. 2. These curves illustrate the effect of pressure with both chemical and physical development for Eastman P. M. C. Bromide Paper No. 1. The results of the three types of physical development are shown separately by displacing the origin along the vertical axis.

was placed between the pin *F* and the pressure ball, so that there were always two spherical surfaces in contact and not one spherical and one flat. The plate-glass block, *G*, which is 3.175 cm thick, was covered with black paper except for a circular opening of 1.75 cm in diameter, in order to prevent the light diffused by the block from affecting the photographic material. This block is singularly free from strains. The tower, *T*, on which the plate-glass block rests, was made in two sections to permit the introduction of screens between the light source and the photographic material. *D* indicates a series of diaphragms which eliminate any light reflected from the sides of the tower and confine the light beam to a circular cross section of 1.75 cm. The path of this light beam was arranged so that it was perpendicular to and concentric with the center of the flattened surface of the pressure ball. A double-ground disk of photographic glass was placed at *Sc* to diffuse the light and to cut down the intensity. The light source *L* was placed in a special housing and attached directly to the tower in such a manner that the possibility of the tower and lamp shifting with respect to each other during the application of high pressures was eliminated. The distance between the center of the lamp and the photographic material is 50 cm. During the course of the experiment two different sources of light were used. They were in turn a 13-watt, frosted Mazda lamp and a 400-watt, clear Mazda lamp; both were burnt at a constant voltage of 108 volts. The current was supplied by a direct-current compound-wound generator with manual field control. Under these conditions the resulting intensity obtained with the 400-watt lamp was approximately 19 times greater than that gained with the 15-watt lamp.

MATERIAL AND DEVELOPMENT

Two types of photographic materials were employed in this experimentation. They were, Eastman P.M.C. Bromide Paper No. 1 and Eastman Portrait Nitrate Film. These materials were developed chemically in the following hydroquinone developer.

Water	3632 cc
Hydroquinone	75 g
Sodium sulphite	240 g
Sulphuric acid	3.5 cc
Potassium carbonate	180 g
Potassium bromide	15 g

The three types of physical development employed were based on the method explained by

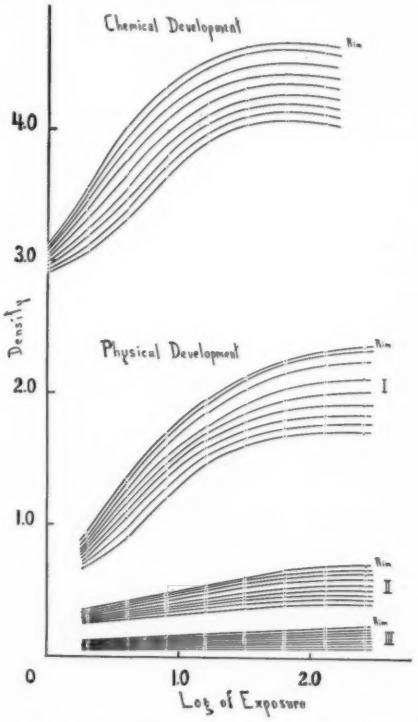

FIG. 3. Effect of pressure ranging from 38.77 to 1356.95 kg/cm² on Eastman Nitrate Film with chemical and physical development.

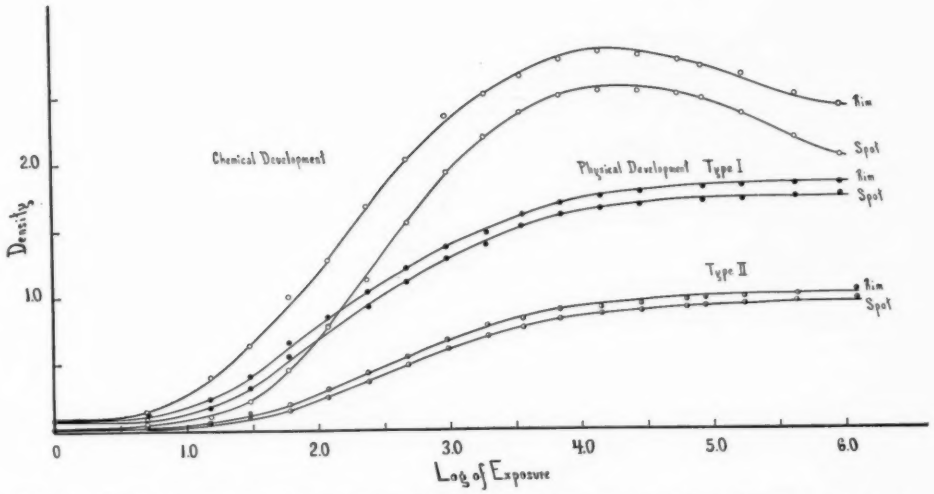

FIG. 4. Effect of pressure on Eastman Portrait Nitrate Film in the region of the first reversal with both chemical and physical development.

Arey[8] and Odell.[9] They were as follows: *Type I.* Photographic material was developed in Arey-Odell formula with fore-bath omitted. *Type II.* A three-minute treatment in an acid sodium thiosulfate bath and a wash in running water for thirty minutes preceded the development of the material in the Arey-Odell formula. *Type III.* A three-minute treatment in a 30-percent plain sodium thiosulfate solution and a wash for thirty minutes in running water preceded development of the material in the Arey-Odell formula.

RESULTS

The exposures for this research were made by placing a sheet of photographic material, 8×10 inches, in a special holder on the pressure machine not shown in Fig. 1. Sheets of this size were employed so that the exposure and development, for each separate group of latent images, would be made under identical conditions. The diffused densities of these images, which are shown graphically in this paper, were measured by means of the "differential photoelectric photometer" described by F. K. Richtmyer.[10]

The curves displayed in Fig. 2 show the effect of pressure and development for Eastman P.M.C. Bromide Paper No. 1 when the weaker light source was used. The curve marked rim represents that region of the image to which no pressure was applied. The other curves show the effect of 38.77, 193.85 and 387.7 kg/cm² of pressure, respectively. In each case a marked decrease in latent image density was obtained. The time of exposure for the chemically developed images ranged from 5 to 50 seconds. After considerable experimentation it was found that if the exposure time, which gave the first chemically formed latent image, was increased by a factor of fifteen a barely perceptible image was obtained with all three types of physical development. Consequently the exposure times for physical development varied from 75 to 750 seconds. A considerable difference in density between the chemical and physical curves may be noted. This seems to be true for all physical development work. By comparing these curves one may say that to obtain a density of 0.1 with both chemical and physical development one would have to increase the exposure time for the physically developed image approximately seven times.

The curves shown in Fig. 3 display the effect of pressure and development on Eastman Portrait Nitrate Film when the weaker light source was employed. In all cases both chemical and physical the application of pressure caused a considerable

[8] L. B. Arey, Am. Phot. 683, Nov. 1934.
[9] A. F. Odell, Eng. Chem. **25**, 877 (1933).
[10] F. K. Richtmyer, Phys. Rev. **6**, 66 (1915).

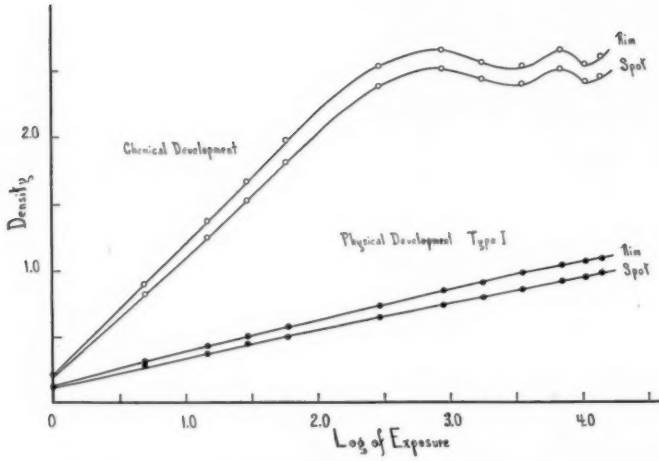

FIG. 5. Effect of pressure on Eastman Portrait Nitrate Film which was exposed to a higher light intensity and then developed chemically and physically.

reduction in latent image density. The amount of reduction depends upon the pressure applied and the type of development employed. The pressures applied in the experiment were, in turn, 38.77, 193.85, 387.7, 581.55, 775.40, 969.25, 1163.10 and 1356.95 kg/cm². The exposure times ranged from 1 to 128 minutes for chemical and 2 to 256 minutes for the physical development. No visible image was obtained for an exposure of one minute with physical development. The latent images which were treated with a solution of 30-percent plain sodium thiosulfate before development gave a set of straight line curves whose densities were considerably less than those obtained with the other types of physical development. This might be accounted for by the fact that the 30-percent sodium thiosulfate solution is strong enough to remove not only the unaffected silver bromide but also the silver which has been liberated by the light action.

The percentage of reduction in pressure region *vs.* rim density of the latent image for an exposure time of 128 minutes and a pressure of 1356.95 kg/cm² was 13 percent for chemical development; 28 percent for Type I physical development; 41 percent for Type II and 68 percent for Type III.

Figure 4 exhibits the extension of the pressure and development effects to the region of reversal for Eastman Portrait Nitrate Film. In this case the pressure was a constant 969.25 kg/cm² and the weaker light source was employed. The exposure time varied from 1 to 950,000 seconds. In all three cases the application of pressure caused a reduction in density. This reduction was most notable with chemical development. The exposure time was sufficient to cause the first reversal with chemical development, while no reversal was displayed in the case of physical development. Especially notable is the fact that on reversal the densities of the pressure areas fall off more rapidly than the densities of the areas not under pressure. Therefore a marked acceleration of reversal is noted in the pressure region. This is in agreement with the findings of Karl Maring, S. J., and Ny Tsi-Ze and his associates.

Figure 5 shows the results obtained when Eastman Portrait Nitrate Film was exposed to the higher light intensity. The pressure employed was 969.25 kg/cm² and the exposure time ranged from 1 to 14,400 seconds. In this time four reversals of the solarization appeared with chemical development and none with physical development. This seems to indicate that we have no reversal where physical development is employed and that the silver liberated by the light action does not combine with the bromine to give reversal.

This same result was obtained in our laboratories with another experiment in which the eight reversal curve, published in the paper

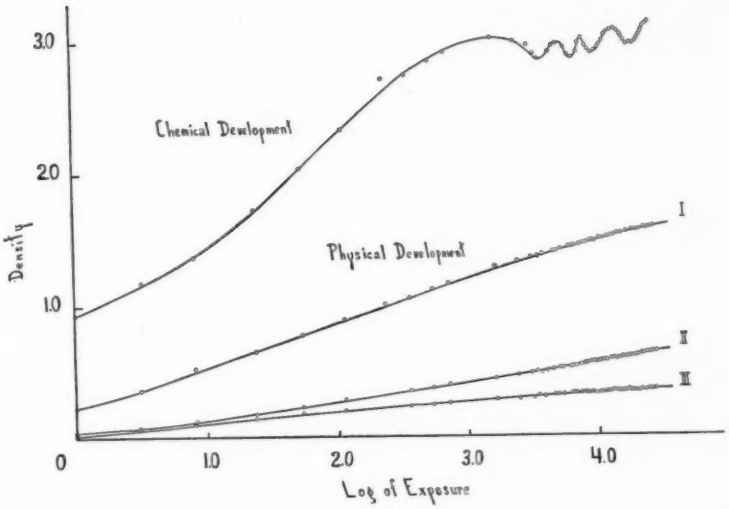

FIG. 6. The influence of development on the region of reversal. Curves I, II and III are the result of the three respective types of physical development. The curve at the top of the figure was obtained with chemical development. The four photographic plates from which the data for these curves were obtained were given identical exposures simultaneously for 26,753 minutes.

entitled "Solarization at Low Intensity,"[11] was reproduced by exposing four photographic plates simultaneously for a period of 26,753 minutes. The apparatus and method of exposure employed were the same as those described in the above-mentioned paper. The results of this experiment are shown graphically in Fig. 6. Curves I, II and III were obtained from three of the exposed plates which were developed physically as described above. The fourth curve, at the top of Fig. 6, was obtained by developing the photographic plate chemically. This curve is similar to the one shown in the "Solarization at Low Intensity" paper. Here again we note the lack of the appearance of reversals with physical development.

Now it is a well-known fact that the density of the physically developed image depends upon the amount of silver liberated in the emulsion by the incident radiation. The application of pressure during exposure diminishes the developed density. If this density depends upon the liberated silver we may assume that less silver is liberated in the pressure region. The actual amount of this silver seems to increase with continued exposure since no reversal has been found with physical development. This leads one to suspect that the reversals which were found with chemical development cannot be accounted for by the recombination theory. The nature of these two developed images (physical and chemical) appears to differ essentially. The chemically developed image does not seem to depend entirely on the colloidal silver liberated by the light during exposure. We might regard the deposition of this silver as incidental but not essential to the formation of the latent image; that is, the process that forms the latent image also liberates silver.

In closing, the author wishes to express her grateful appreciation to Dr. Franklin E. Poindexter, of the Physics Department of St. Louis University, for suggesting and assisting with the development of this research.

[11] A. J. Reardon and H. P. Griggs, J. Opt. Soc. Am. **24**, 331 (1934).

A Theoretical Treatment of the Two-Quanta Hypothesis as Applied to the Photographic Reciprocity Law Failure*

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A PHOTOGRAPHIC emulsion is qualified by the intrinsic sensitivity of its individual silver halide grains and by its size-frequency characteristics. If a be the size (area) of a grain, the latter property is determined by a function $f(a)$ such that $f(a)da$ gives the number, per unit area of the plate, of grains whose size falls within the limits a to $a+da$. The "intrinsic sensitivity," so called in my previous publications and denoted by ϵ, is defined, independently of any assumptions about the mechanism of the action of light upon the silver halide crystals, as follows. Let n be the total number of quanta of monochromatic light thrown upon every unit area of the plate or, statistically, an the number of quanta per grain. The *probable* or, in a numerous assemblage of equal grains, the average number of quanta photoefficiently absorbed by a grain is some fraction of the pure number an, and it is precisely this fraction, ϵ, which is defined as intrinsic sensitivity of the grain. This does not at all imply the reality of the picturesque image of the grain as a target and of the quanta as slender arrows or darts hitting it, geometrically, now here and now there, but amounts merely to defining ϵ as the photographically efficient absorption coefficient per unit area of the grain. Nor does it imply that ϵ is necessarily independent of the size a itself. Only experiment seems to indicate that sometimes it is so, while it depends essentially on the wave-length of the quanta. The adjective "photographically efficient" is necessary for distinguishing this coefficient from the coefficient, say κ, of total or general light absorption (with or without photographic effects), which again may be defined per unit area of a grain, so that κan is the probable number of quanta absorbed by a grain without qualification, while ϵan is the probable number of photographically efficient absorbed quanta. The latter, then, is just a fraction of the former. Numerous experimental determinations made in these Laboratories during the last year have shown that, for various emulsions, ϵ ranges from a fraction of one percent up to almost 15 percent of the general absorption κ, the ratio $\epsilon : \kappa$ increasing, on the whole, with decreasing wave-length.

In what follows the qualification "photographically efficient" will be frequently dropped for the sake of brevity, but will be always subintended when we speak of the absorption, by a grain, of one, two or more quanta.

To approach our present subject, let $y=\epsilon an$ be the probable number of absorbed quanta per grain, corresponding to a total exposure of n quanta, spread over the whole exposure time arbitrarily. Then, as will be recalled, the probability that a grain (of size a) shall absorb r or more quanta is

$$P=1-e^{-y}\left[1+y+\frac{1}{2!}y^2+\cdots+\frac{1}{(r-1)!}y^{r-1}\right].$$

If such an absorption is assumed to be the necessary and the sufficient condition for the developability of a grain, this will also be the probability that the grain shall become developable and, if the emulsion consists of equal grains, the corresponding photographic density D will be proportional to P. But, after an obvious expansion of e^{-y}, the lowest term of P is found to be proportional to y^r or n^r, so that the density will be initially proportional to the rth power of the exposure. If the emulsion consists of unequal grains, the simple proportionality of D to P is replaced by a more complicated expression or function of the exposure, but the remarkable property just mentioned remains invariant. In fact, as has been shown in a previous paper,[1] if r quanta are required for the developability of a grain, the density is initially proportional to

* Communication No. 744 from the Kodak Research Laboratories.

[1] L. Silberstein and A. P. H. Trivelli, J. Opt. Soc. Am. 28, 441 (1938), especially p. 454.

the rth power of the exposure, whatever the form of the size-frequency function $f(a)$ of the emulsion. Now, most of the emulsions so far investigated in these Laboratories have shown, when exposed to visible or near ultraviolet light, an initial proportionality of density to *the square of the exposure*, thus calling for the assumption of the absorption of *two quanta* as the *minimum* required for the developability of a grain.[2] Accordingly, this assumption has been adopted throughout in our latest publications and will also be retained in the present paper. The corresponding elementary probability formula, to be frequently referred to in the sequel, is

$$P=1-\epsilon^{-y}(1+y), \tag{1}$$

where y stands for $\epsilon a n$ and is thus proportional to *the total exposure*, such being the meaning of n (in quanta as units). In expanded form, $P=\frac{1}{2}y^2-\frac{1}{3}y^3+\cdots$, starting with the squared exposure, in accordance with the general remark.

As a matter of fact, the initial proportionality of the observed density to the squared exposure shows only that a considerable fraction of the grains present are satisfied, each, with two quanta, while others might call for three or more quanta. For a superposition of several series, one starting with y^2, another with y^3, and so on, would still give a series starting with y^2. But a close scrutiny of many sensitometric curves has shown that the introduction of such higher ingredients, for a retouching of the theoretical curves, is not at all necessary, so that the pure two-quantic assumption may be retained throughout the discussion.

Let us, then, consider more closely the corresponding probability formula (1). To gain a clear insight into its photographic implications, suppose that the emulsion consists of a number of grains all equal as to size a and sensitivity ϵ, and disregard the effect of the gradual absorption of light in traversing the whole layer. Then the exposure conditions are the same at all depths and the resulting photographic density[1] is simply

$$D=D_m[1-\epsilon^{-y}(1+y)], \tag{1.1}$$

where D_m is the extreme density obtainable with the given emulsion coating, and thus a constant number. Hence, the density D, as expressed by (1.1), depends on y alone or, since the factor ϵa is fixed, on n only, the *total* number of quanta thrown upon unit area, no matter how these are distributed over the duration t of the exposure. If, for instance, the intensity of light is kept constant during the whole exposure, when the variable in (1) takes on the form

$$y=it,$$

the resulting density D would not depend on the chosen intensity or time, but only on their *product*. Now, such a simple behavior which, after Roscoe, is referred to as the Reciprocity Law, holds only approximately, within certain narrow limits and at moderate intensities, while, in general, the density is found to depend in an intricate way on the two factors, i and t, taken separately, any such departure from Roscoe's law being alluded to as a reciprocity failure. If we keep the total exposure it constant and, starting with very dim light, increase the intensity (shortening the time), then the density D increases steadily until a certain, so-called "optimal" intensity is reached, beyond which the density begins to drop. The well-established, and extensively studied, facts of reciprocity failure show us, then, that the probability P for a grain to become developable by a given total exposure y decreases with decreasing intensity i, when i is below the "optimum," i.e., that some at least of the grains which have absorbed two quanta remain yet undevelopable when the frequency of the arriving quanta is lessened* or, in other words, when the time elapsing between the two absorptions exceeds some finite limit.

The modification of our previous assumption, necessary in order to account for the facts of reciprocity failure, only *below* the optimal intensity for the present, is thus obvious.

We shall, therefore, restrict our original assumption by postulating that a grain shall be made developable by absorbing two light quanta *within a certain finite time interval*, τ, a charac-

[2] In the case of x-ray exposures, a *single* quantum makes a grain developable, as has been conclusively proved by microphotographic experiments. Phil. Mag. **9**, 787 (1930).

* For, the measure of *the intensity* of radiation, which in classical theory was defined by the squared amplitude of electromagnetic oscillations, is now wholly reduced to *the number of quanta* striking or crossing a surface per unit area *and per unit time*.

teristic of the grain itself, and that the grain shall remain undevelopable in spite of the double absorption if this time limit is exceeded.[3]

In an assemblage of grains (emulsion), the interval τ may be either equal for all or vary from grain to grain. It is enough, however, to treat thoroughly the case of a unique, fixed interval. The case of any desired frequency distribution $\varphi(\tau)d\tau$ of the intervals among the grains is then easily dealt with by integration over the parameter τ.

This leads us to consider the following interesting problem in probabilities.

A total of n_1 quanta strike unit area during the time t_1 at a uniform rate (constant "intensity"). The probable number of quanta absorbed, per grain, being

$$y_1=\epsilon a n_1=it_1,$$

what is the probability, P, that a grain shall have absorbed two (or more) quanta *within an interval* τ?

If the total exposure time does not exceed this interval, in fine, if $t_1\leqslant\tau$, the answer is obviously $P=1-e^{-y_1}(1+y_1)$, as in (1), depending on the total exposure y_1 only.

If, however, $t_1>\tau$, the interval τ can be placed within t_1 in an infinity of ways, and the probability P becomes an intricate function of y_1 and i or t_1 and i, the more so the greater the multiple of τ contained in t_1. Manifestly, the complication increases when we pass from one such interval of t_1 to the next higher one. Let us consider the second interval,

$$\tau\leqslant t_1\leqslant 2\tau,$$

and let us, first, solve the problem by an exhaustive enumeration of all possibilities, to be replaced presently by a less wearisome method.

The total exposure time t_1 being fixed, let t be any of its instants and $y=it$. Put also, for brevity, $\eta=i\tau$, a constant. The probability of *no* absorption up to t is e^{-y}; the probability of a single absorption* in the following dt is dy. Hence, the probability of a *first* absorption between y and $y+dy$ is

$$e^{-y}dy.$$

The probability of one or more absorptions within a following interval $\leqslant\eta$ is

1. $1-e^{-\eta}$ for $y_1-y>\eta$ or $y<y_1-\eta$

and

2. $1-e^{-(y_1-y)}$ for $y_1-y<\eta$ or $y>y_1-\eta$.

The probability of *no* absorption within this interval is, for case 1, just $e^{-\eta}$.

Finally, the probability of two or more absorptions within the yet remaining interval $y_1-(y+\eta)$, possible only in case 1, since there is no "remaining interval" in case 2, is

$$1-e^{y+\eta-y_1}(1+y_1-y-\eta).$$

It remains to collect these probabilities for all possible positions of the instant t, i.e., to integrate over y. Thus, the required probability P that a grain shall absorb two (or more) quanta, photoefficiently, within any interval τ contained in t_1, or η contained in y_1, is, for the case $\eta\leqslant y_1\leqslant 2\eta$,

$$P=\int_0^{y_1-\eta}e^{-y}(1-e^{-\eta})dy+\int_{y_1-\eta}^{y_1}e^{-y}(1-e^{-y_1+y})dy$$

$$+e^{-\eta}\int_0^{y_1-\eta}[1-e^{y+\eta-y_1}(1+y_1-y-\eta)]e^{-y}dy.$$

The simple integrations are easily effected. Some pairs of terms cancel and, if the now superfluous subscript 1 is dropped, the complete probability receives the neat expression

$$P=1-e^{-y}\{1+y+\tfrac{1}{2}(y-\eta)^2\},\quad \eta\leqslant y\leqslant 2\eta. \quad (2)$$

The exponential and the first two terms of its factor are exactly as in (1), valid for the first

[3] A similar assumption, though in an implicit form, has been made by W. J. Albersheim, J. Soc. Mot. Pict. Eng. **32**, 73–104 (1939). Albersheim assumes an exponential "fading of the activated" grains, which amounts to assuming an infinite range of intervals τ with an exponential distribution function $\varphi(\tau)$. This dispenses him from entering into the delicate probability problem and permits him to treat the relations summarily by means of a pair of ordinary differential equations. Of these, however, one is an essentially incorrect rendering of Mr. Albersheim's own assumption of a "blocking time." We shall return to this subject in the sequel.

The concept of timed quantum absorptions has already been used some years ago, in a particular problem of reciprocity failure, by J. H. Webb and the writer, Phil. Mag. **18**, 1 (1934).

* Needless to say, the probability of a *double* absorption within dt is evanescent, i.e., of the order of dt^2 or dy^2.

interval, functions of the exposure y only. The third term contains $\eta = i\tau$ or the intensity, and thus expresses a reciprocity failure. It depresses the probability, the more so the dimmer the light. The probability function is, so far, represented by its two branches, (1) for the first and (2) for the second interval of the variable y. Since the third term vanishes at their junction, $y=\eta$, the two branches pass into each other continuously. Moreover, $P'(\eta)=\eta e^{-\eta}$ for both, so that the probability curve has neither a break nor a cusp at the junction. (Only P'' or the curvature changes abruptly, but a drawing would scarcely disclose it.)

Now for the third and further intervals. An exhaustive enumeration of the possibilities would soon become prohibitively cumbersome. It may be replaced by a more elegant and equally rigorous method, which will yield the successive branches directly. In fact, suppose that the total exposure time t is extended by dt or y by dy. Let $dP=P'(y)dy$ be the corresponding increment of the probability. Imagine for the moment a great number N of equal grains and think of P as the number of grains made developable divided by N. Then NdP, the increment of the number of developable grains, is clearly equal to the product of $idt=dy$ into the number of grains left undevelopable at the instant t *less* the number of grains which were left undevelopable at $t-\tau$ and which have *not* absorbed between $t-\tau$ and t.

In symbols, and removing the common factor Ndy,

$$P'(y)=1-P(y)-[1-P(y-\eta)]e^{-\eta}, \quad \text{for any } y>\eta. \tag{3}$$

This, then, is a general relation between the derivative and the function itself at the instant t or y and its *past* value $P(y-\eta)$, or what I may be permitted to call a *hystero-differential* equation for the unknown function P, in contrast to the usual differential equation which binds a derivative or derivatives of various orders with the value of the function at *the same* instant. If we disregard for the moment our knowledge of a whole branch, (1), of the unknown function P, then a hystero-differential equation such as (3) is, in a certain sense, equivalent to an ordinary linear differential equation of an infinitely high order. For the function remains undetermined unless we prescribe (arbitrarily) an infinity of point-data or, in fact, a complete branch of P, either in one or in several pieces, of total extension η. Apart from photography, such equations would seem to deserve the mathematician's as well as the physicist's attention. They are, no doubt, more simple but, perhaps, not less interesting than Volterra's "integro-differential" equations which, alongside of derivatives, contain an integral taken over a whole stretch of the function's past or future.

Turning to our problem, to solve Eq. (3) put

$$P(y)=1-e^{-y}Q(y); \tag{4}$$

then

$$P'(y)=[Q(y)-Q'(y)]e^{-y}=e^{-y}Q(y) - e^{-(y-\eta)}Q(y-\eta)\cdot e^{-\eta},$$

or

$$Q'(y)=Q(y-\eta), \quad \text{for any } y>\eta. \tag{5}$$

This, then, is a much simpler hystero-differential equation for $Q(y)$. Instantaneous rate of increase equal to an antedated value of the function. The solution of our particular problem by means of this equation is immediate. But before turning to this point, I ask the Editor's permission to make a few general remarks which may interest some readers of this Journal.

Suppose that, apart from the numerical value of η, no data concerning Q are available. Let it be known only that it is differentiable (just once), of course. Then we cannot invoke Taylor's theorem which would otherwise enable us to write the relation (5) at once $Q'=Q-\eta Q' +(\eta^2/2)Q''\cdots$, exhibiting it as a differential equation of order ∞. But, in spite of this prohibition, it is easy to show that to all relevant purposes it is equivalent to such an equation. For (5) is certainly satisfied by

$$Q=c\cdot e^{my},$$

where c is an arbitrary coefficient, provided that m is a root of the equation

$$me^{m\eta}=1. \tag{6}$$

Now, if η is real and positive, say, this transcendental equation has (just) one real root and an infinity of conjugate pairs of complex roots. Everyone of these roots, m_κ, gives a solution Q

of the stated form, and since (5) is linear,

$$Q=\sum_{\kappa=1}^{\infty} c_\kappa e^{m_\kappa y}, \tag{7}$$

with arbitrary c_κ, is again its solution. This, then, leaves an *infinity* of coefficients c_κ at our free disposal, which proves the intended equivalence. Since there are, moreover, no double roots, the infinite series (7) is also the complete solution of Eq. (5). In fact, it can be adapted to a whole branch of Q arbitrarily prescribed within an η-interval, say from $y=0$ to $y=\eta$, provided only that $Q'(\eta)=Q(0)$. I may mention, without proof, that all coefficients in (7) are then uniquely determined, *viz.*, by

$$\frac{1+\eta m_\kappa}{m_\kappa}c_\kappa=Q(\eta)+\int_0^\eta Q(y)e^{-m_\kappa y}dy, \tag{8}$$

the roots m_κ being virtually known numbers.[4]

Returning to our subject, let us recall that in the first interval, by (1) and the definition (4) of Q,

$$Q(y)=1+y, \quad 0\leqslant y\leqslant \eta, \tag{9.1}$$

and let us, once more, consider the second interval. If y is within the second, then $y-\eta$ is in the first interval, so that, by (5) and (9.1),

$$Q'(y)=1+y-\eta,$$

whence

$$Q(y)=y+\tfrac{1}{2}(y-\eta)^2+\alpha,$$

where α is a constant. Now, claiming the continuity of P and thus that of Q at $y=\eta$, we have $\eta+\alpha=1+\eta$, so that $\alpha=1$ and

$$Q(y)=1+y+\tfrac{1}{2}(y-\eta)^2, \quad \eta\leqslant y\leqslant 2\eta, \tag{9.2}$$

in perfect agreement with the result (2) found by an exhaustion of the possibilities.

Next, if y is in the third, $y-\eta$ is in the second interval, so that, by (5) and (9.2),

$$Q'(y)=1+y-\eta+\tfrac{1}{2}(y-2\eta)^2,$$

whence, integrating and claiming the continuity of Q at $y=2\eta$,

$$Q(y)=1+y+\frac{1}{2!}(y-\eta)^2+\frac{1}{3!}(y-2\eta)^3, \quad 2\eta\leqslant y\leqslant 3\eta. \tag{9.3}$$

[4] More details are given in my purely mathematical paper "On a Hystero-Differential Equation," Phil. Mag. in press.

Similarly for the fourth interval, and so on. The structure of Q for any y is now obvious. If m be any positive integer and $m\eta<y<(m+1)\eta$, then

$$Q(y)=1+y+\frac{1}{2!}(y-\eta)^2+\cdots+\frac{1}{(m+1)!}(y-m\eta)^{m+1}. \tag{9}$$

This, together with (4), $P=1-e^{-y}Q$, is the complete solution of the probability problem.

The probability function is represented, separately for each interval of its argument, by polynomials (9), with $\eta=i\tau$ as parameter. Notice that, while at $y=\eta$ only P and P' are continuous, at $y=2\eta$ the function and its first two, at $y=3\eta$ the function and its first three derivatives are continuous, and so on, so that the successive branches of the function are more and more intimately welded together.

Since $\eta/y=\tau/t$, where t is the total exposure time, the complete probability formula given by (9) and (4) may also be written, for any $m\eta\leqslant y\leqslant(m+1)\eta$,

$$P=1-e^{-y}\sum_{\kappa=0}^{m+1}\frac{y^\kappa}{\kappa!}\left[1-\frac{(\kappa-1)\tau}{t}\right]^\kappa\equiv 1-e^{-y}Q, \tag{10}$$

thus bringing into evidence the exposure *time*, always through τ/t, separated from the *total exposure* y, which marks a reciprocity failure. The intensity of light can be introduced by recalling that $t=y/i$. Manifestly, the function Q is, for any nonvanishing τ, always smaller than $e^y=1+y+\frac{1}{2}y^2+\cdots$, so that P is contained between 0 and 1. For $y\to\infty$ both Q and e^y increase indefinitely, but the latter more rapidly, so that their quotient Qe^{-y} tends to zero and P to unity (all grains made developable), no matter how low the intensity i. If we put $\tau=0$, then, as is seen also directly from (5), $Q=e^y$ and P vanishes for any y. In fact, the probability of a double absorption within an evanescent time τ is nil or evanescent of the order $i^2\tau^2$. If, on the other hand, $\tau=\infty$, when there is no restrictive timing of the two absorptions, $Q=1+y$ permanently, and we fall back upon the older formula. The effect of any finite interval τ consists in

depressing the probability P, the more so the lower the intensity or its product into τ.

Formula (10) is now ready for photographic applications, always with the express understanding, stated above, that we limit ourselves to light *below* the optimal intensity. In order to account for the facts of reciprocity failure beyond this limit, another restriction as to the timing of the two absorptions (working oppositely to τ) would have to be imposed, from which we prefer to abstain for the present. It seems better to deal first as thoroughly as possible with the lower intensities.

If N_a be the number of grains of size a present, per unit area of the base, the number k of such grains made developable by the exposure y is PN_a or

$$k = N_a(1-e^{-y}Q), \tag{11}$$

where Q is as in (10). Actually, $Q=Q(y,i)$, where i measures the intensity kept constant during the whole exposure.

The first derivative, $P'(y)$, of the probability function has also a simple meaning. In fact, by what was said in constructing Eq. (3), $P'(y)$ is the probability that a grain remains undevelopable at the end of the exposure y, but has absorbed a single quantum within the last interval τ. To borrow a short name from Albersheim, let us call such grains *activated grains*. Our assumption may then be restated by saying that a grain remains activated only through a fixed interval of time and, unless it absorbs a second quantum, relapses into its natural state at the expiration of this time.* Thus, if k' be the number of activated grains, of size a, left over at the end of the exposure, we have simply $k'=N_aP'$ or

$$k' = N_a(Q-Q')e^{-y}. \tag{12}$$

This, of course, gives us only the total number of activated grains without telling us how the dates of their activation are distributed in time. It is enough, however, to know that these dates are all spread *over the last τ-interval* only, although by no means uniformly. Thus, if the light is shut off and a time τ passes, the activated grains will be all gone or will have relapsed into their normal state, and we shall be left with k developable and N_a-k intact grains.

Before proceeding with our general subject we may make a very simple but, perhaps, not uninteresting application of this conclusion. Suppose that our N_a grains are given an exposure $y_1=it_1$ and then, after a lapse of time just equal to or greater than τ, another exposure at the same intensity, $y_2=it_2$. The result of the first exposure will be

$$k_1 = N_a[1-e^{-y_1}Q(y_1)]$$

developable and, after the lapse of τ, $N_a-k_1 = N_ae^{-y_1}Q(y_1)$ intact grains. The effect of the second exposure alone will then be

$$k_2 = N_ae^{-y_1}Q(y_1)[1-e^{-y_2}Q(y_2)]$$

more developable grains. Thus the joint result $k(y_1, y_2)=k_1+k_2$ of the two exposures will be

$$k(y_1, y_2) = N_a[1-e^{-(y_1+y_2)}Q(y_1)Q(y_2)].$$

On the other hand, the result of a unique, uninterrupted exposure $y=y_1+y_2$, applied to an equal sample of grains, would be, always by (11),

$$k(y) = k(y_1+y_2) = N_a[1-e^{-(y_1+y_2)}Q(y_1+y_2)].$$

Without calculation one sees that this must be always greater than the first result, for part of the light's work has been wasted by the interruption. Write $\Delta k = k(y_1+y_2)-k(y_1, y_2)$. Then what we may call *the splitting-effect* will be

$$\Delta k = N_ae^{-y}[Q(y_1)Q(y_2)-Q(y_1+y_2)], \tag{13}$$

where $y=y_1+y_2$. By what has just been said, we know beforehand that this effect, Δk, must be *positive*, that is to say, an actual loss in k, and thus in photographic density D, due to the splitting of an exposure. At the same time, the formula (13) gives us a property of our Q-function which it would be rather hard to prove, in general, from the definition, (10), of this function, namely,

$$Q(y_1)Q(y_2) > Q(y_1+y_2), \tag{14}$$

for any (nonvanishing) y_1, y_2. For N_ae^{-y} in (13) is essentially positive.

* We need not consider at all the question in what that "activated" state of the silver halide crystal consists, in terms of electronic or wave-mechanical concepts. Even if we did, this would not change one iota in the effect of our assumption upon the resulting expressions for the photographic density or other measurable quantities. The only relevant thing is the presence of an interval such as τ, and its finite duration.

If, for instance, not only y_1, $y_2<\eta$, but also $y_1+y_2\leqslant\eta$, then

$$Q(y_1)=1+y_1,\quad Q(y_2)=1+y_2,$$
$$Q(y_1+y_2)=1+y_1+y_2,$$

so that the difference of the two expressions is, simply, $y_1y_2>0$, and the splitting-effect receives the elegant expression

$$\Delta k=N_a e^{-y}\cdot y_1y_2, \tag{13.1}$$

proportional to the product of the instalment-exposures. It attains its maximum (with $y=$const.), for $y_1=y_2=y/2$, *viz.*,

$$\Delta k=\tfrac{1}{4}N_a y^2e^{-y}, \tag{13.2}$$

the effect corresponding to two equal instalments. The product y^2e^{-y} itself has its maximum at $y=2$ (which in our case implies $\eta>1$), giving, as the greatest possible splitting effect, $\Delta k=N_a/e^2$ or almost one-quarter of $k=N_a(1-3/e^2)$ produced by the uninterrupted exposure. If, to mention another example, $y_1=y_2=\eta$, then

$$Q(y_1)Q(y_2)=(1+\eta)^2,\quad Q(y_1+y_2)=1+2\eta+\tfrac{1}{2}\eta^2,$$

so that the difference is $\frac{1}{2}\eta^2$, and $\Delta k=\frac{1}{2}N_a e^{-2\eta}\eta^2$. Exactly the same relations would hold, in an ideally homogeneous emulsion, for the loss in density, ΔD, due to splitting of the exposure, and the proportionate splitting-effect $\Delta D/D$ for an emulsion of any size-frequency distribution ought to be much of the same order as above, i.e., up to about one-quarter or one-fifth, at any rate, an easily discoverable effect. Of course, if the pause between the two instalment-exposures is shorter than τ, only a part of the effect ΔD ought to manifest itself.

Formula (13.1), with $N_a=f(a)da$, holds for every size-class of grains. Multiplying by the size a, integrating over all sizes present in an emulsion, and inserting the factor $M=\mathrm{Log}\,e$, we have the loss in photographic density D due to splitting of the exposure y,

$$\Delta D=M\int_0^\infty af(a)y_1y_2e^{-y}da.$$

For an emulsion of *exponential* frequency distribution, $f(a)=(N/\bar a)e^{-a/\bar a}$, the integration is easily effected. If we write, ultimately, $y=\epsilon\bar a n$, the integral becomes (for constant ϵ)

$$\frac{N\bar a y_1y_2}{(1+y_1+y_2)^4}\int_0^\infty x^3e^{-x}dx=\frac{6N\bar a y_1y_2}{(1+y)^4},$$

and since $MN\bar a=D_m$, the extreme density obtainable with the given emulsion coating, the splitting-effect is

$$\Delta D=\frac{6D_m y_1y_2}{(1+y)^4},\quad y=y_1+y_2. \tag{13.3}$$

In particular, for an equipartition of exposure, $y_1=y_2=\frac{1}{2}y$,

$$\Delta D=\tfrac{3}{2}D_m y^2/(1+y)^4. \tag{13.4}$$

The total density corresponding to the uninterrupted exposure is[1] $D(y)=D_m y^2(3+y)/(1+y)^3$. The effect attains its maximum for $y_1=y_2=\frac{1}{2}$ or $y=1$, namely, $\frac{3}{32}D_m$. Since, at the same time, $D(y)=D(1)=\frac{1}{2}D_m$, the maximum splitting-effect is

$$\Delta D=\frac{3}{16}D(1), \tag{13.5}$$

or almost one-fifth of the full density, and thus ought to be easily detected.

Let us now return to the general probability formula (10), valid for any exposure time t and total exposure $y=n\epsilon a=it$, in order to apply it to an emulsion of any size-frequency distribution.

The number of grains of size a to $a+da$ made developable by an exposure y is $P(y)f(a)da$. Thus, if we write, for the total area of the grains,

$$S=\int_0^\infty af(a)da,$$

and $D_m=MS=MN\bar a$ for the extreme density, the density D corresponding to the exposure y will be expressed by

$$\frac{D}{D_m}=1-\frac{1}{S}\int_0^\infty af(a)Qe^{-y}da, \tag{14}$$

where Q is as in (10). If we assume that, within a given emulsion, τ is independent of the grain size a, then only the factor y^κ in Q contains a, and

$$\frac{D}{D_m}=1-\frac{1}{S}\sum_{\kappa=0}^{m+1}\frac{1}{\kappa!}\left[1-\frac{(\kappa-1)\tau}{t}\right]^\kappa I_\kappa, \tag{15}$$

where

$$I_\kappa = \int_0^\infty a f(a) y^\kappa e^{-y} da. \tag{16}$$

It remains to evaluate this integral for any integer κ, including 0, for a given distribution function $f(a)$.

It may suffice, for the present, to consider an *exponential* emulsion, that is to say,

$$f(a) = (N/\bar{a}) e^{-a/\bar{a}} = (S/\bar{a}^2) e^{-a/\bar{a}},$$

where $\bar{a}$ is the average grain size and N, the number of grains over unit area of the base. Write $\bar{y} = n\epsilon\bar{a}$. Then, if ϵ be independent of a,

$$\frac{I_\kappa}{S} = \frac{(n\epsilon)^\kappa}{\bar{a}^2} \int_0^\infty a^{\kappa+1} e^{-(1+\bar{y})a/\bar{a}} da$$

or, putting $x = (1+\bar{y})a/\bar{a}$,

$$\frac{I_\kappa}{S} = \frac{\bar{y}^\kappa}{(1+\bar{y})^{\kappa+2}} \int_0^\infty x^{\kappa+1} e^{-x} dx = \frac{\bar{y}^\kappa}{(1+\bar{y})^{\kappa+2}} (\kappa+1)!$$

Thus, by (15), and if we now drop the bar over y, so that y will henceforth stand for $n\epsilon\bar{a}$,

$$\frac{D}{D_m} = 1 - \sum_{\kappa=0}^{m+1} (\kappa+1) \left[1 - \frac{(\kappa-1)\tau}{t}\right]^\kappa \frac{y^\kappa}{(1+y)^{\kappa+2}}. \tag{17}$$

This holds for any exposure time,

$$m\tau \leqslant t \leqslant (m+1)\tau.$$

The exponential function has disappeared (by averaging over all sizes) and the resultant expression for the density is not more complicated than Q itself for a single grain. This is a peculiarity of an exponential $f(a)$. In developed form, and adding together the constant term 1 and the first two terms of the sum,

$$\frac{D}{D_m} = \frac{y^2(3+y)}{(1+y)^3} - \frac{3y^2}{(1+y)^4}\left(1 - \frac{\tau}{t}\right)^2 - \frac{4y^3}{(1+y)^5}\left(1 - \frac{2\tau}{t}\right)^3 - \cdots. \tag{17a}$$

TABLE I.

$y =$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1	2	4	8	16	32
$D_{1/4} =$	0.034	0.104	0.222	0.379	0.553	0.708	0.826	0.901	0.953
$D_{1/2} =$	0.034	0.104	0.259	0.453	0.642	0.787	0.884	0.938	0.970
$D_1 =$	0.034	0.104	0.259	0.500	0.704	0.843	0.922	0.962	0.983
$D =$	0.034	0.104	0.259	0.500	0.741	0.896	0.966	0.990	0.998

This is, for every finite t, a finite polynomial, its last term having the factor $(1-m\tau/t)^{m+1}$. If $t \leqslant \tau$, we fall back upon our old formula,

$$D = D_m y^2(3+y)/(1+y)^3.$$

If $\tau < t \leqslant 2\tau$, we have to add only the next term, expressing through its factor $(1-\tau/t)^2$ a reciprocity failure. If t exceeds 2τ, the next term comes in, and so on. At $t = \tau, 2\tau$, etc., not only D, but also its derivative $D'(y)$ is continuous, so that the complete sensitometric curve (17) has nowhere a break or a cusp.

Recalling that $y = it$, where i (for a fixed $\epsilon\bar{a}$) measures the constant intensity of light, we may write

$$\frac{D}{D_m} = \frac{y^2(3+y)}{(1+y)^3} - \frac{3}{(1+y)^4}(y - i\tau)^2 - \frac{4}{(1+y)^5}(y - 2i\tau)^3 - \cdots. \tag{17b}$$

All terms $(y - \kappa i\tau)^{\kappa+1}$ are positive, so that the existence of a restricting finite τ-interval *depresses the density*, the more so the weaker the light.* To form a tangible idea of this effect, consider some particular numerical values of τi. Since the D, Log y curve represented by the first term alone has its inflection point at $y = 1$, terminating a good half of the whole curve, a considerable effect can be expected only if τi does not much exceed unity and, still more so, if $\tau i < 1$. Let us, then, take the three cases $\tau i = 1$, $\frac{1}{2}$, and $\frac{1}{4}$. A few power-of-two "steps" will suffice for each case. If we write D_1, $D_{1/2}$, and $D_{1/4}$ for the corresponding densities and take, for the moment, D_m as unit, then, by (17b), the sets of densities are as in Table I. The last row contains the densities represented by the first term of (17b) alone which would be valid throughout for $i\tau = \infty$ and which hold, at any rate, up to $y = 32$ for any $i\tau \geqslant 32$. The corresponding four curves are drawn in Fig. 1, with the exposures $y = it$ spaced logarithmically, in the

* When τi tends to zero, the negative terms form an infinite series whose sum is just equal to the first term, so that D tends to zero. In fact, recalling that, for $x < 1$, $1 + 2x + 3x^2 + \cdots = 1/(1-x)^2$, one finds easily

$$\frac{y^2}{(1+y)^4}\left\{3 + \frac{4y}{1+y} + \frac{5y^2}{(1+y)^2} + \cdots\right\} = \frac{y^2(3+y)}{(1+y)^3}.$$

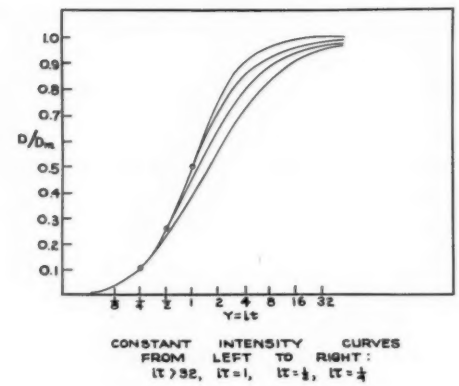

FIG. 1. Constant intensity curves. From left to right: $i\tau>32$, $i\tau=1$, $it=\frac{1}{2}$, $i\tau=\frac{1}{4}$.

usual way. They coincide all up to $y=\frac{1}{4}$, where the $\tau i=\frac{1}{4}$ curve branches off tangentially. Similarly, the curves $\tau i=\frac{1}{2}$ and $\tau i=1$ branch off, without a cusp, at $y=\frac{1}{2}$ and $y=1$. Beyond the bifurcation points, the density D corresponding to a given exposure y is the smaller the lower the intensity i. Equivalently, the total exposure y or it required to produce a given density is the greater the weaker the light.

The reciprocity failure is frequently represented by *constant-exposure* curves, that is to say, by sets of densities corresponding to varying intensities at constant total exposure it. The equation of any such curve follows from (17b) by putting $y=$const. It may suffice to consider in detail one such curve, say $y=it=1$. Its equation is

$$\frac{D}{D_m}=\frac{1}{2}-\frac{3}{16}(1-\tau i)^2-\frac{4}{32}(1-2\tau i)^3 -\frac{5}{64}(1-3\tau i)^4-\cdots. \quad (17.1)$$

For $\tau i=1$, the density attains its highest value, $\frac{1}{2}D_m$, which (without further assumptions) it would retain also for all greater values of τi. Thus, $i=1/\tau$ plays, so far, the part of the optimal intensity, with this total exposure. For $1>\tau i\geqslant\frac{1}{2}$ the next term comes into play, for $\frac{1}{2}>\tau i\geqslant\frac{1}{3}$ one more term, and so on. Thus, for geometrically decreasing intensities, we have the following set of steadily decreasing densities.

$$y=1\begin{cases}\tau i & = 1 & \frac{1}{2} & \frac{1}{4} & \frac{1}{8} & \frac{1}{16} & \frac{1}{32} & \frac{1}{64}\\ D/D_m & =0.500 & 0.453 & 0.379 & 0.290 & 0.203 & 0.130 & 0.076.\end{cases}$$

The corresponding curve is drawn in Fig. 2. It ascends with increasing i up to $\frac{1}{2}D_m$, where it is continued, without a cusp, by the horizontal straight line. (The purpose of the dotted line beyond $\tau i=1$ is to indicate qualitatively that, for intensities exceeding the "optimum," actual experiment shows a gentle decrease of density.) Since D, as well as $\partial D/\partial i$ remains continuous at $\tau i=1, \frac{1}{2}, \frac{1}{3}$, etc., the curve is continuous and has nowhere a cusp.

We have, so far, assumed that the interval τ is the same for all grains (of a given emulsion), in other words, that all activated grains have the same "life" τ. Suppose now, more generally, that the length of this interval is distributed among the grains, regardless of their size, according to some law, so that $\varphi(\tau)d\tau$ is the fraction of all grains whose life is contained between τ and $\tau+d\tau$, where $\varphi(\tau)$ is any given function satisfying the condition

$$\int_0^\infty \varphi(\tau)d\tau=1.$$

The interval τ enters into the general expression (15) for the density only through the coefficients

$$(1-\tau/t)^2, \quad (1-2\tau/t)^3, \quad \text{etc.,}$$
$$\text{generally } (1-\kappa\tau/t)^{\kappa+1},$$

which appear also unmodified in the resulting density formula for any emulsion, as e.g., in (17) or (17a). Thus, in order to extend our formulae to the general case now considered, we have only to integrate each of these coefficients over the corresponding ranges of the "life" τ. Let t be the total duration of the exposure (at constant intensity i, as before). Then *all* grains, whatever their life τ, will contribute to the first term in the density formula, not containing τ, as e.g., the first term in (17a). Thus, and since

$$\int_0^\infty \varphi(\tau)d\tau=1,$$

this term will remain unmodified. The next

term, with the coefficient $(1-\tau/t)^2$, comes into play only when t exceeds τ, and has, therefore, to be integrated over all τ ranging from 0 up to t. The term with $(1-2\tau/t)^3$ appears only when t exceeds 2τ, and has thus to be integrated only from $\tau=0$ up to $\frac{1}{2}t$, the next term from $\tau=0$ up to $\frac{1}{3}t$, and so on. In fine, any of our coefficients, say

$$c_\kappa=(1-\kappa\tau/t)^{\kappa+1},$$

has now to be replaced by

$$c_\kappa'=\int_0^{t/\kappa}(1-\kappa\tau/t)^{\kappa+1}\varphi(\tau)d\tau. \qquad (18)$$

This settles the question. If the life-statistics, $\varphi(\tau)$, is prescribed, all the required coefficients will be found by evaluating the integral in (18) for any positive integer κ.

With the coefficients thus determined we shall have, e.g., for an emulsion of exponential size distribution of grains, by (17a), the density formula

$$\frac{D}{D_m}=\frac{y^2(3+y)}{(1+y)^3}-\frac{3y^2c_1'}{(1+y)^4}-\frac{4y^3c_2'}{(1+y)^5}-\frac{5y^4c_3'}{(1+y)^6}-\cdots, \qquad (19)$$

the reciprocity failure being here wholly expressed by the presence of c_1', c_2', and so on, since these coefficients are, ultimately, functions of the exposure time t alone (with the averaged τ as parameter).

The statistical function $\varphi(\tau)$ is simply related to the function, say ψ, which expresses the decrease in time of the number of activated grains, or briefly, the "fading" of the activated grains. For, if this number is reduced, after a time τ, by the factor $\psi(\tau)$, we have, manifestly,

$$\varphi(\tau)=-\psi'(\tau)=-d\psi/d\tau.$$

Let, for instance, as has been assumed by Albersheim,[3] the activated grains fade out *exponentially*, with a "fading time" α, that is to say, let $\psi(\tau)=e^{-\tau/\alpha}$. Then our statistical function is again an exponential, *viz.*,

$$\varphi(\tau)=\frac{1}{\alpha}e^{-\tau/\alpha}, \qquad (20)$$

where $\alpha=\bar{\tau}$ is then *the average* value of τ or the average life of activated grains. For,

$$\int_0^\infty \tau\varphi(\tau)d\tau=\alpha.$$

Let us evaluate the coefficients (18) for this particular distribution of the intervals τ. Let s be the total exposure time with the average life $\bar{\tau}=\alpha$ as unit, i.e.,

$$s=t/\bar{\tau},$$

and let us introduce the integration variable $x=1-\kappa\tau/t$ instead of τ itself. Then (18) becomes

$$c_\kappa'=\binom{\kappa}{s}^{\kappa+1}e^{-s/\kappa}\int_0^{s/\kappa}x^{\kappa+1}e^x dx$$

or, after an integration by parts,

$$c_\kappa'=1-(\kappa+1)\binom{\kappa}{s}^{\kappa+1}e^{-s/\kappa}\int_0^{s/\kappa}x^\kappa e^x dx,$$

where $\kappa=1$, 2, and so on. Now, the indefinite integral is

$$\int x^\kappa e^x dx=e^x[x^\kappa-\kappa x^{\kappa-1}+\kappa(\kappa-1)x^{\kappa-2}-\cdots+(-1)^\kappa\kappa!],$$

so that

$$c_\kappa'=1-(\kappa+1)\binom{\kappa}{s}^{\kappa+1}\left\{\binom{s}{\kappa}^\kappa-\kappa\binom{s}{\kappa}^{\kappa-1}+\kappa(\kappa-1)\binom{s}{\kappa}^{\kappa-2}-\cdots+(-1)^\kappa\kappa!(1-e^{-s/\kappa})\right\}. \qquad (21)$$

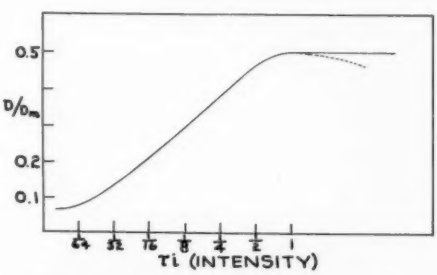

FIG. 2. Constant exposure curve. $y=it=1$.

Thus, for instance,

$$c_1' = 1 - 2\left(\frac{1}{s}\right)^2 \{s - (1 - e^{-s})\},$$

$$c_2' = 1 - 3\left(\frac{2}{s}\right)^3 \left\{\left(\frac{s}{2}\right)^2 - s + 2(1 - e^{-s/2})\right\},$$

$$c_3' = 1 - 4\left(\frac{3}{s}\right)^4 \left\{\left(\frac{s}{3}\right)^3 - 3\left(\frac{s}{3}\right)^2 + 3.2\frac{s}{3} - 6(1 - e^{-s/3})\right\},$$

and so on. These are the rigorous values of the coefficients, valid for any exposure time $s = t/\bar{\tau}$. If this amounts to many units ($\bar{\tau}$), the coefficients all approach unity, the negative terms in (19), as we saw before, cancel the first, positive term, and the density D approaches zero. But what is of main interest is the case of *small*, fractional values of s. Since the factor of the bracket in (21) has $s^{\kappa+1}$ in the denominator, one might think that the coefficients c_κ' become then enormous. But this is only an appearance. Developing the last term in (21), it is found that the whole bracketed expression is itself of the order of $s^{\kappa+1}$, namely, up to $s^{\kappa+3}$,

$$\frac{1}{\kappa+1}\left(\frac{s}{\kappa}\right)^{\kappa+1} - \frac{1}{(\kappa+1)(\kappa+2)}\left(\frac{s}{\kappa}\right)^{\kappa+2},$$

so that, ultimately, up to higher terms in s,

$$c_\kappa' = s/\kappa(\kappa+2) = (t/\bar{\tau})/\kappa(\kappa+2), \qquad (21')$$

i.e., $c_1' = s/3$, $c_2' = s/8$, $c_3' = s/15$, and so on.*

Substituting these coefficients in (19), we have for the density produced in an exponential emulsion by an exposure $y = it$, of short duration t compared with $\alpha = \bar{\tau}$,

$$\frac{D}{D_m} = \frac{y^2(3+y)}{(1+y)^3} - \frac{t}{\alpha}\cdot\frac{y^2}{(1+y)^4}\left[1 + \frac{1}{2}\frac{y}{1+y} + \frac{1}{3}\frac{y^2}{(1+y)^2} + \frac{1}{4}\frac{y^3}{(1+y)^3} + \cdots\right].$$

But since the bracketed series, with

$$x = y/(1+y) < 1,$$

converges and has the sum

$$-\frac{1}{x}\log(1-x) = \frac{1+y}{y}\log(1+y),$$

this density formula becomes

$$\frac{D}{D_m} = \frac{y^2(3+y)}{(1+y)^3} - \frac{t}{\alpha}\cdot\frac{y\log(1+y)}{(1+y)^3} \qquad (22)$$

or

$$\frac{D}{D_m} = \frac{y^2}{(1+y)^3}\left[3 + y - \frac{\log(1+y)}{\alpha i}\right], \quad y < \alpha i, \qquad (22')$$

valid up to higher terms in t/α or $t/\bar{\tau}$. If t approaches or exceeds $\bar{\tau}$ considerably, we have to apply formula (19) with the values (21) of the coefficients. If, on the other hand, the exposure is very short compared with $\bar{\tau}$ (or αi is a great number), we fall back upon the first term of (22) or our older formula, as was to be expected. The role of the average interval $\bar{\tau}$ is thus brought clearly into evidence.

At the same time we see that, for $y = \text{const.}$, the density D tends to its highest value *asymptotically*, for $t \to 0$ or $i \to \infty$, which contradicts the main experimental fact of reciprocity failure, namely, the existence, for every constant exposure, of a *finite* optimal intensity. Thus, an exponential fading of the activated grains, equivalent to an exponential distribution of intervals down to $\tau = 0$, is ruled out. More generally, only such distribution functions $\varphi(\tau)$ are admissible which vanish below a certain finite τ_m. For then and only then will there be a finite optimal intensity, $i = y/\tau_m$.

This asymptotic behavior, expressed by (22) for a heterogeneous emulsion, holds also for the fundamental function $Q(y)$ which gives the probability P or the fraction, k, of grains made developable, $k = 1 - e^{-y}Q(y)$. With a unique interval τ for all grains, this function is expressed by (10) or, briefly,

$$Q = \sum_{\kappa=0}^{m+1} \frac{1}{\kappa!} y^\kappa c_{\kappa-1}.$$

Hence, for any distribution $\varphi(\tau)$ of intervals τ,

* The complete expansion is

$$c_\kappa' = \frac{s}{\kappa(\kappa+2)}\left[1 - \frac{s}{\kappa(\kappa+3)} + \frac{s^2}{\kappa^2(\kappa+3)(\kappa+4)} - \cdots\right].$$

ranging from 0 to ∞,

$$Q(y)=\sum_0^\infty \frac{1}{\kappa!}y^\kappa c'_{\kappa-1}, \tag{23}$$

where the coefficients c_κ' are determined by (18). If, in particular, this distribution is exponential, as in (20), the coefficients c_κ' depend on $s=t/\alpha=y/\alpha i$ alone and are given rigorously, for any value of $s=t/\alpha$, by (21) or, in developed form, by

$$c_\kappa'=\frac{s}{\kappa(\kappa+2)}\left[1-\frac{s}{\kappa(\kappa+3)}+\frac{s^2}{\kappa^2(\kappa+3)(\kappa+4)}-\cdots\right], \tag{24}$$

where $\kappa=1, 2, 3$, etc., while $c_0'=c'_{-1}=1$. Introducing (24) into (23) and collecting the contributions to each power of y,† one finds

$$Q(y)=1+y+\frac{1}{\alpha i}\left[\frac{y^3}{3!}+\frac{y^4}{4!}\left(\frac{1}{2}-\frac{1}{\alpha i}\right)+\frac{y^5}{5!}\left(\frac{1}{3}-\frac{1}{2\alpha i}+\frac{1}{\alpha^2 i^2}\right)-\cdots\right], \tag{25}$$

and the corresponding proportionate number of developable grains is

$$k=1-e^{-y}Q(y). \tag{25.1}$$

Now, owing to the coefficient $1/\alpha i$ of the bracketed expression, very much as in (22′), the function Q attains its lowest value for $i=\infty$, so that, for constant exposure y, the photographic effect k would increase asymptotically with increasing intensity, thus contradicting the experimental facts.

This case, of an exponential $\varphi(\tau)$, is interesting, mathematically at least, in that it is the only one in which the delicate probability problem of timed absorptions can be obviated and the hystero-differential equation can be replaced by an ordinary differential equation of, moreover, the simplest kind. Such is precisely the case treated by Albersheim who has assumed an *exponential fading* of the activated grains, equivalent to an exponential $\varphi(\tau)$. In fact, let k' be the number of activated grains at any instant. Then, with this assumption, the time rate of decrease of k' is just proportional to the value of k' at the same instant, namely, equal to k'/α. Thus, while $dk/dt=ik'$ or $dk/dy=k'$, the net rate of increase of k' receives, as in Albersheim's treatment, the obvious expression

$$\frac{dk'}{dy}=(1-k-k')-\frac{dk}{dy}-\frac{1}{i\alpha}k'=1-k-\left(2+\frac{1}{i\alpha}\right)\frac{dk}{dy}$$

or

$$\frac{d^2}{dy^2}(k-1)+\frac{1+2\alpha i}{\alpha i}\frac{d}{dy}(k-1)+k-1=0,$$

a simple differential equation. Since $k=k'=0$ for $y=0$, its solution is

$$k=1-\frac{m_1e^{-m_2y}-m_2e^{-m_1y}}{m_1-m_2}, \tag{26}$$

where m_1, m_2 are the roots of the quadratic $m^2-[(1+2\alpha i)/\alpha i]m+1=0$. This, in fact, is Albersheim's main formula, (18),[3] without the "blocking time" (*vide infra*) and apart from the specific meaning of our variable $y=it=na\epsilon$. But as has been just explained, this formula, being based on an exponential fading, must lead to an asymptotic increase of k with intensity (instead of giving a finite optimal intensity), and is thus wholly inadmissible. It seems that Albersheim has failed to see this conclusion because his formula, (26) above, is in appearance entirely different from (25.1) with (25) and does not show explicitly the role of αi as divisor. But if we write

$$e^{-m_2y}=e^{-y}\cdot e^{-(m_2-1)y}$$

$$=e^{-y}\left[1-(m_2-1)y+\frac{1}{2!}(m_2-1)^2y^2-\cdots\right],$$

and similarly for e^{-m_1y}, then (26) assumes at once the form

$$k=1-e^{-y}\left\{1+y+\frac{1}{\alpha i}\left[\frac{y^3}{3!}-\frac{y^4}{4!}\cdot\frac{1}{\alpha i}+\cdots\right]\right\}, \tag{26′}$$

which coincides with (25) rigorously up to y^3 inclusive and differs from it, in an irrelevant

† Since the lowest term in $\frac{1}{2!}y^2c_1'$ contains y^3, there is no y^3-term in the resulting series.

way, only in the coefficients of the higher terms. The essential point is that k tends again to its highest value $1-e^{-y}(1+y)$ asymptotically, for $i\to\infty$, in just the same way as in (25), (25.1).

This shows conclusively that an exponential fading of the activated grains or an exponential distribution $\varphi(\tau)$ of intervals is ruled out. We might still introduce any range of τ's bounded by a nonvanishing shortest τ-value. The simplest plan, however, is to retain our original assumption of a single interval τ common to all grains within a given emulsion, though varying from emulsion to emulsion. Then the function Q is as in (10) and

$$k=1-e^{-y}\left\{1+y+\frac{1}{2!}(y-i\tau)^2+\frac{1}{3!}(y-2i\tau)^3+\cdots\right\} \quad (27)$$

gives the proportionate number of developable grains of any size-class. As before, $y=it$ stands for the total exposure, and if the exposure time t is contained between $m\tau$ and $(m+1)\tau$, the last term of the polynomial is a power of $y-mi\tau$. For $y=$const. the optimal intensity is $i=y/\tau$ or, the *optimal exposure time*, $t=\tau$, at least to a first approximation, that is to say, apart from the fact that our k remains stationary, while experiment shows a slow but distinct decline of k below the optimal time. The next question to be considered is that as to the actual length of the interval τ for various emulsions. Albersheim speaks repeatedly, but without convincing experimental support, of the fading time, i.e., α or $\bar{\tau}$, as being "measured in hours." But since any formula based on an exponential fading leads necessarily to an asymptotic increase of k with intensity, it is actually impossible to determine the value of the implied time $\bar{\tau}$ from any experimental sensitometric or constant-exposure curves which essentially contradict such a behavior. At any rate, the interval τ appearing in our last formula need by no means run into hours. On the contrary, there are good reasons for attributing to it the order of a very few seconds down to a moderate fraction of a second. In fact, the interval τ, if not rigorously, is at any rate approximately equal to the optimal time, and the observed optimal times are all of the said order. Thus, for the experimental emulsion No. 1340,[5] exposed to 6.25 m.c.s., the optimal intensity lies between 6 and 25 m.c. and, therefore, the optimal time between 1 and $\frac{1}{4}$ second, and at the exposure 3.12 m.c.s. it is decidedly nearer to $\frac{1}{4}$ sec. Again, with the density $D=1$ as the peak of the constant-exposure curve, the optimal time is 2 sec. for Portrait Panchromatic emulsion, 1 sec. for W and W Hypersensitive Panchromatic (plate), $\frac{1}{2}$ sec. for Contrast Cine Positive as well as for Commercial Film, further, $\frac{1}{3}$ sec. for Eastman 33 Plate, and even as short as 1/10 and 1/20 sec. for Cine Positive and Process Film, respectively. These examples will suffice to show that the interval τ appearing in formula (27) must be attributed a length of the order of one-tenth up to one or a few seconds only. Some grains of an emulsion may remain activated for several hours, perhaps, as would seem to follow from the increase of the splitting-effect ΔD (described above), found so far in a single experiment, by an extension of the time gap between the two instalment exposures from three to sixteen hours. Such grains, however, cannot affect the shape of a sensitometric curve, and it would be useless to encumber our formula with the corresponding quadratic and higher terms, since these would remain inoperative unless the exposure itself is protracted over many hours. In other words, only the comparatively short-lived grains, characterized summarily by a single τ of the order of a second, will contribute to a perceptible reciprocity failure. Let these grains form some fraction, β, of all grains present. Then the quadratic and higher terms in (27) will receive the factor β, approximately a constant fraction,* while the first two terms of the bracket and the exponential factor will remain unmodified, reducing (27) to

$$k=1-e^{-y}\left\{1+y+\frac{\beta}{2!}(y-i\tau)^2+\frac{\beta}{3!}(y-2i\tau)^3+\cdots\right\}, \quad (28)$$

[5] Investigated for its sensitivity in J. Opt. Soc. Am. **29**, 67 (1939).

* Rigorously, β will be a slowly increasing function of y, since for $y>i\tau$ the developability of the long-lived grains is more probable, so that the short-lived grains will form an increasing fraction of all grains left, at any stage, undevelopable.

for any size-class of grains. Similarly, the corresponding density formula (17b), found by integration for an emulsion of exponential size-frequency distribution, becomes

$$\frac{D}{D_m}=\frac{y^2(3+y)}{(1+y)^3}-\frac{3\beta}{(1+y)^4}(y-i\tau)^2 - \frac{4\beta}{(1+y)^5}(y-2i\tau)^3-\cdots. \quad (29)$$

In (28), y or it stands for $n\epsilon a$ and in (29), for $n\epsilon\bar{a}$.

Equation (28) and, in particular, its integrated form (29) will serve as the working formula for further investigations of the theory in relation to experimental data. At the present stage the formula can claim only to account for the observed facts, up to the optimal intensity, in a merely *qualitative* way.

Note on High Intensities

In order to account for the decrease of the photographic effect when, at constant exposure, the optimal intensity is exceeded, Albersheim[3] restricts the time elapsing between the two quantum absorptions by a *lower* limit which he calls the "blocking time (t_b)," and which we shall denote by σ. The net meaning of his assumption is that a grain becomes developable only if the time elapsing between the two absorptions exceeds σ. If that time is shorter than or just equal to σ, the grain shall remain undevelopable. A direct implication is that, if the total exposure time is $\leqslant\sigma$, there is no photographic effect to be expected, no matter what the intensity of the radiation. Since photographs have been obtained with exposure times down to 10^{-5} or even 10^{-6} sec., σ can be only a minute fraction of a second, and therefore, very small in comparison with the fading time, τ. This being kept in mind, the hypothesis is in no way unreasonable and gives an interesting and perfectly natural means for securing a reduction of the photographic effect of quanta arriving in *too* rapid a tempo or of light at too high intensity. Unfortunately, however, Albersheim's mathematical formulation of his own concept is incorrect.

If k and k' are the numbers of developable and of activated grains at any time t, then, in absence of a restrictive blocking time, as we saw, $dk/dt=ik'$ or, in Albersheim's nomenclature, k' divided by the "electron time" $(1/i)$. Now, if there be a blocking time σ, he says that dk/dt is just k' "divided by the electron time *plus* the blocking time" and writes accordingly (since his C is soon enough identified with 1)

$$dk/dt=k'/(\sigma+1/i)=ik'/(1+\sigma i), \quad (A)$$

which is manifestly wrong. So much so that his resultant formula, (18),[3] does not give $k=0$ for $t\leqslant\sigma$, as it should if the mathematical rendering of his assumption were correct. In fact, Mr. Albersheim derives from (18) for "extremely high intensities" (p. 97) an equation,

$$D=D_m(1-e^{-t/\sigma}),$$

which ought to show him the inconsistency. But he misreads it into "indicating that a *minimum* time proportional to σ is required for the formation of the latent image." Palpably, this equation indicates no such thing. On the contrary, it gives for $t=\sigma$ the huge density $D_m(1-1/e)$, instead of zero, and continues to give positive densities right down to $t=0$, contradicting the very meaning of the blocking time.

The correct effect of a blocking time, or lower time limit σ between the two absorption acts, is readily found. It can be determined rigorously by an exhaustion of the possibilities, as in our τ-problem above, and more simply as to detail. Let t_1 be the whole exposure time and $y_1=it_1$. Since σ is very much shorter than τ and is effective only for t_1 comparable with σ, we may as well assume that $t_1\leqslant\tau$. Then, if t be any instant of the exposure, the probability of a first absorption within the interval t to $t+dt$ is, as before, dye^{-y}. This leaves the time $t_1-t-\sigma$ for a second efficient absorption, provided that $t<t_1-\sigma$. The probability of a further absorption during this remaining time is $1-e^{-(y_1-y-\sigma i)}$. The required probability that the grain shall be made developable by the exposure y_1 is the product of these two probabilities summed over all possible dates t of the first absorption, that

is to say, from $t=0$ up to $t_1-\sigma$ or $y=0$ up to $y_1-\sigma i$,

$$P(y_1)=\int_0^{y_1-\sigma i} e^{-y}(1-e^{-y_1+y+\sigma i})dy.$$

The integral is instantly evaluated. Thus, and dropping the superfluous subscript 1,

$$P(y)=1-e^{-(y-\sigma i)}[1+y-\sigma i]. \qquad (30)$$

This is the required probability or (proportionate) number k of developable grains of a given size-class. It holds for any exposure time $t\leqslant\tau$, or exposure $y\leqslant\tau i$. If t/σ is enormous, the supplementary terms σi may be omitted, but become effective when t is shortened and made comparable with σ. For $t=\sigma$, $y=\sigma i$, and $P=k=0$ (no photographic effect), as it should be. For $t<\sigma$ the formula gives a negative probability, expressing emphatically enough the absence of developable grains.

At the same time, since the number of activated grains is $k'=ye^{-y}$, while $k=P$, we have the relation

$$dk/dt=e^{\sigma i}(1-\sigma/t)ik', \qquad (31)$$

which shows once more the incorrectness of (A). If, in particular, σ/t is negligible, we have, up to $(\sigma i)^2$,

$$\frac{dk}{dt}=(1+\sigma i)ik'=k'\Big/\left(\frac{1}{i}-\sigma\right)$$

or k' divided by "electron time" *minus* blocking time, just the opposite of Albersheim's surmise.

Formula (30) holds rigorously up to $t=\tau$. The effect of σ upon the quadratic and higher terms which appear only when t exceeds τ, 2τ, and so on, is manifestly negligible. Thus, the complete formula (28), with $\beta=1$ for the present, becomes

$$k=1-e^{-(y-\sigma i)}\left\{1+(y-\sigma i)+\frac{1}{2!}(y-\tau i)^2+\frac{1}{3!}(y-2\tau i)^3+\cdots\right\}. \qquad (32)$$

This holds for all intensities i and all exposure times $t=y/i$. Consider a constant-exposure curve, $y=$const. For evanescent intensity i or enormous t/τ the bracketed expression is

$$1+y+\frac{1}{2!}y^2+\cdots=e^y,$$

and $k=0$. With decreasing exposure time t (increasing i), the value of this expression decreases and k increases steadily. When t falls just below 2τ, the bracket is reduced to its first three terms. With always decreasing exposure time, k continues to increase and attains its maximum for $\partial k/\partial t=0$ or, up to higher powers of σ/τ, for

$$i_0=\frac{y}{t_0}=\frac{y}{\tau}\left(1-\frac{1}{2}\frac{\sigma}{\tau}\right)$$

or

$$t_0=\tau(1+\tfrac{1}{2}\sigma/\tau), \qquad (33)$$

which is indiscernible from $t_0=\tau$. This, then, is the optimal exposure time (and i_0 is the optimal intensity). Henceforth, k decreases with decreasing t. When t is shortened down to and below τ, we are left with

$$k=1-e^{-(y-\sigma/t)}[1+y(1-\sigma/t)].$$

For $t=\tau$, just beyond the maximum, k does not differ perceptibly from $1-e^{-y}(1+y)$ and, for still shorter times, decreases steadily, but at first very slowly, towards zero for $t=\sigma$. This descent may be much too slow, even in comparison with the rather gentle experimental descent of the curve. In fact, a decrease below $k_{\max}$ cannot become perceptible unless the exposure time is shortened down to $t=100\sigma$, from $t_0=\tau=1$ second, say (such being the optimal times in many actual cases). Now, according to the record of shortest efficient exposure, $\sigma=10^{-5}$ sec., at the utmost. Thus, a first decrease of density would become perceptible only if $t=10^{-3}$ sec. or if the intensity were made a thousand-fold of the optimal intensity i_0. Actually, however, a decrease of density is already observable for $i=16i_0$ or, perhaps, $64i_0$. If, therefore, σ is, indeed, of the order of 10^{-5} or 10^{-6} sec. for all grains of an emulsion, it has but a purely theoretical interest, being incapable of accounting for the observed facts. A possible way to overcome this difficulty would consist in assuming

that, while σ is 10^{-6} sec., or even shorter, for some grains of the emulsion, in compliance with the said record, there is a considerable percentage of grains whose blocking time is a hundred or a few hundred times longer. What is ultimately required is a ratio $\sigma : \tau$ of the order 10^{-3}.

At any rate, both concepts, of a lower and an upper time restriction of the absorption process, for which full credit must be given to Albersheim, seem to offer considerable interest and to deserve further constructive attention.

ACKNOWLEDGMENT

My thanks are due to Mr. A. P. H. Trivelli and Dr. J. H. Webb of these Laboratories for helpful information.

A Four-Filter Photoelectric Colorimeter

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(Received August 16, 1939)

THE development of fluorescent lamps created a need in our laboratory for routine color ratings. To meet this need, we constructed a photoelectric colorimeter. This instrument consisted of three filters mounted on a slide in front of a General Electric lightmeter cell. The filters were selected to make the cell-plus-filter spectral sensitivity curve approximate the I.C.I. $\bar{x}$ function[1] for wave-lengths greater than 0.505μ, the $\bar{y}$ function and the $\bar{z}$ function, respectively. Three-filter photoelectric colorimeters use the same filter for the Z response and for the portion of the X response due to radiation of wavelengths less than 0.504μ. This compromise makes it difficult to obtain I.C.I. color coordinates with such an instrument unless all of the colors to be rated lie within a relatively small range. Since the conversion factors (or additive corrections) depend not only on the color but also[2] on the spectral distribution giving the color, the instrument must be calibrated separately for each spectral distribution. The use of a single set of conversion equations or nomograms in rating colors which cover a wide range may introduce errors too large to be tolerated.

TABLE I. *Filter data and required cell area.*

FILTER	RESPONSE	GLASS* NUMBER	MELT NUMBER	THICKNESS (MM)	CELLS NEEDED
A	*X* (λ's $>0.504\mu$)	330 397	11-9-31 11-19-35	9.54 3.50	2.00
B	*Y*	330 428	11-9-31 7-20-35	3.36 2.82	0.82
C	*Z*	*GG3* 554 555 038†	27198 2-13-35 2-7-36	0.45 2.49 3.82	0.92
D	*X* (λ's $<0.504\mu$)	*GG3* 554 555 038†	27198 2-13-35 2-7-36	0.45 5.05 5.96	0.27

* Corning glasses, except for Jena GG3.
† Corning No. 038 samples had 41 percent transmission for $\lambda 0.415\mu$; they should have transmitted 54 percent.

CONSTRUCTION AND ADJUSTMENT OF INSTRUMENT

Our experience with a three-filter photoelectric colorimeter, together with the article on this subject by van den Akker,[2] led us to construct a four-filter instrument. Some of the specifications[3] for this instrument are given in Table I. If the melt specified for a filter component is not available, the required thickness must be recomputed, for the melt actually used. The receivers are five General Electric lightmeter cells. The last column of the table gives the approximate multiple of the area of a single cell

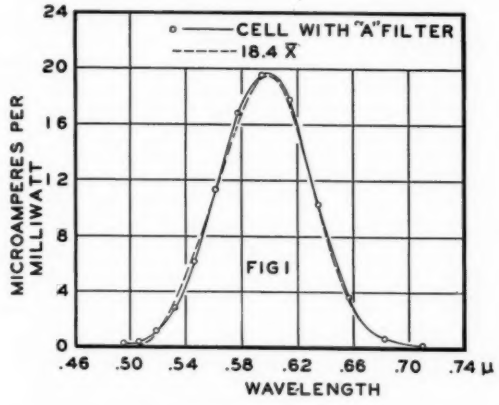

FIG. 1. Solid line, spectral sensitivity of cell with *A* filter; dashed line, 18.4 $\bar{x}$.

which must be exposed through each filter if the meter readings are to be proportional to the I.C.I. color coordinates.

The spectral sensitivities of the cell-filter combinations are shown on Figs. 1 to 4 by the solid

[1] D. B. Judd, J. Opt. Soc. Am. **23**, 362 (1933).
[2] See J. A. van den Akker, J. Opt. Soc. Am. **27**, 401 (1937).
[3] The filters are modifications of those selected by Dr. R. S. Hunter, of the Colorimetry Section of the National Bureau of Standards, for a three-filter instrument. See J. Opt. Soc. Am. **28**, 179 (1938).

lines.[4] The dashed lines on these figures give the $\bar{x}$, $\bar{y}$, and $\bar{z}$ curves (multiplied by suitable constants) which the solid lines should duplicate. In Figs. 1 and 2, the two curves are in close agreement on the long wave-length side of the maximum, but differ considerably on the short wave-length side. In Figs. 3 and 4, the agreement is much less satisfactory, but could be improved by the use of thinner pieces of No. 038 glass. (See note at bottom of Table I.)

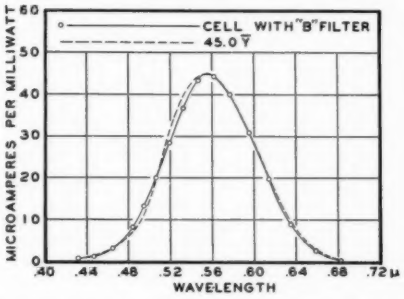

FIG. 2. Solid line, spectral sensitivity of cell with *B* filter; dashed line, 45.0 $\bar{y}$.

The spectral sensitivities of two of the cells used in the colorimeter are shown by Fig. 5. Photoelectric cells taken at random will be apt not to have the spectral sensitivity curve required for use with the filters specified in Table I. The cells for use with filters *A* and *B* must have spectral sensitivity curves practically identical to the corresponding ones in Fig. 5. If such cells cannot be found, one should compute the filter thicknesses which, when used with the available cells, will give the best fit to the ideal curve. All of the G. E. lightmeter cells that we have tested are suitable for use with filters *C* and *D*. These filters have high transmission over such a narrow wave-length range that variations, from cell to cell, in the average slope of the spectral sensitivity curve for this wave-length region have little effect. If any of the 26 cells which we have tested within the last two years were used with either of these filters, the greatest deviation of the relative sensitivity curve from that for the

[4] The cell with the *C* filter has a small sensitivity (less than 1 percent of maximum) for radiation of wave-lengths 7000–7600A. This is not shown on Fig. 3 and is negligible in most cases. With a red fluorescent lamp a small *Z* reading is obtained, although the true *Z* rating for this lamp is zero.

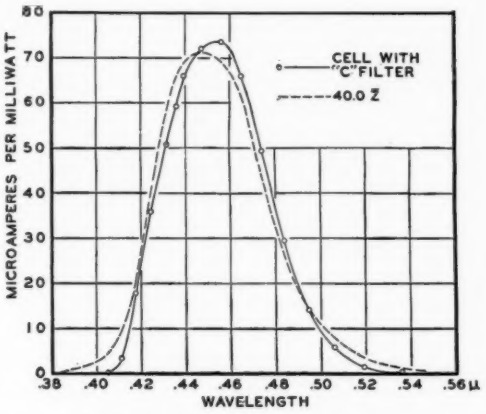

FIG. 3. Solid line, spectral sensitivity of cell with *C* filter; dashed line, 40.0 $\bar{z}$.

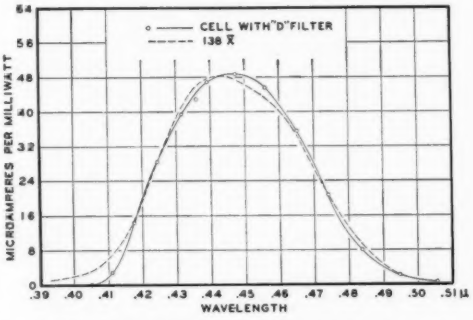

FIG. 4. Solid line, spectral sensitivity of cell with *D* filter; dashed line, 138 $\bar{x}$.

filter plus the average cell would not exceed 3 percent of the maximum sensitivity. Compensation for differences between the absolute sensitivities obtained with different cells is obtained by adjustment of the exposed areas.

The cell-filter combinations are at the back of a wooden box provided with suitable diaphragms. The dimensions of this box are not of general interest, since it was designed for use with nothing but 18″ fluorescent lamps. It was painted dull black both inside and out. The lamp is provided with a black background in order to prevent the entrance of light from the room into the colorimeter. The aperture at the front of the box is just large enough to permit radiation from all parts of the lamp to strike all of the cells. Since no shutter is used, the cells and filters are illuminated continuously while the lamp is

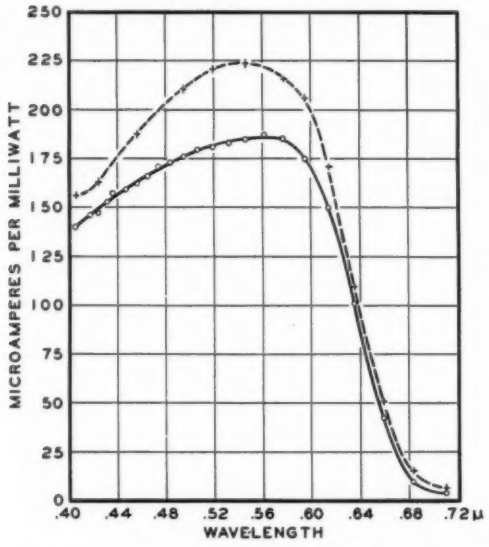

FIG. 5. Spectral sensitivity of two G. E. lightmeter cells. Solid line: cell #466–5, used with *B* filter; dashed line: cell #396–10, used with *A* filter.

warming up. This would be undesirable if the irradiation were more intense because temperature changes of 10 or 15°C would affect the filter transmissions and cell sensitivities appreciably.

The filters and diaphragms are permanently mounted in front of the cells. The cell-filter arrangement shown in Fig. 6 puts the center of gravity of the cell or cells used for each reading within three centimeters of the optical axis. Each diaphragm is merely a strip of metal shading one end of the cell. In the case of cell *D*,* both ends were shaded in order to have the illuminated area near the middle of the cell. The proper position for the diaphragms may be computed if spectral-sensitivity curves with ordinates in comparable terms are available for the particular cell-filter combinations used in an instrument. In making these computations, allowance must be made for the shunting action of cells which are used in parallel.

If calibrated sources are available, the diaphragms may be adjusted by trial. First, cell *D* is connected to one terminal of a three-position selector switch and one of cells *A* is connected to each of the other terminals. Using any suitable source, one determines the ratio of the current furnished by cell *D* to the sum of the currents furnished by cells *A*. The diaphragm on cell *D* is adjusted until this ratio is equal to the ratio of the short wave-length component X_s to the long wave-length component X_L of the *X* rating of the source. These components are given by the following equations:

$$X_s = \int_{0.380}^{0.504\mu} E\bar{x}d\lambda \quad \text{and} \quad X_L = \int_{0.504}^{0.760\mu} E\bar{x}d\lambda,$$

where $Ed\lambda$ is the radiant flux in the wave-length interval between λ and $\lambda+d\lambda$, and $\bar{x}$ is a "distribution coefficient" of the 1931 I.C.I. system.[1]

When the diaphragm on cell *D* has been adjusted, the cell *D* and cells *A* are all connected in parallel, so that the current corresponding to the *X* response is obtained with a single meter reading. The selector switch is wired to connect the meter to this combination of cells, to cell *B*, to cell *C*, or to an open-circuit contact. The diaphragms used with filters *B* and *C* should now be adjusted until the instrument gives the correct color coordinates for a source of the type which is to be rated most frequently with the instrument.

ERRORS IN "INSTRUMENTAL" COLOR COORDINATES

The differences between the color coordinates indicated by one instrument, after final adjustment, and those computed from spectral intensity data are given in Table II. The range from the largest negative to the largest positive error is 0.043. Since the average deviation of a

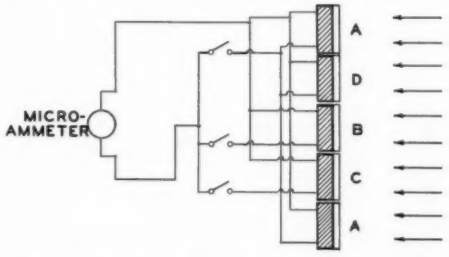

FIG. 6. Diagram of cell-filter arrangement and of electrical circuit.

* The letter used in Table I to designate a filter will be used to designate the diaphragm, the cell or cells, and the circuit used with this filter.

computed color coordinate value from the mean of the values computed from two to four independent sets of spectral intensity data was 0.002, the errors listed in Table II must be chiefly due to deviations of the sensitivity curves of the cell-filter combinations from the ideal curves. If the colors to be tested lie within relatively narrow ranges, the instrumental errors may be practically eliminated by the use of standard lamps. The additive corrections indicated by the results on the standard lamps are applied to the test lamps.

TABLE II. *Lumen factors and errors* in color coordinates for fluorescent lamps of various colors.*

Lamp Type	Indicated Minus True Value			Lumens ÷ Y Reading
	x	y	z	
Daylight	−0.001	−0.002	0.003	54.
White	.007	− .006	− .001	53.
Green	.013	− .001	− .012	55.
Pink	.009	− .008	− .001	55.
Blue	− .001	.008	− .007	52.
Gold	.004	− .014	.010	54.
Red	.003	− .023	.020	54.

* These are the errors obtained when no corrections are applied to the instrument readings. If the corrections indicated by standard lamps of each color are applied, much greater accuracy can be secured. (See section entitled "Precision of Results.")

Precision of Results

All tests of this instrument have been made with fluorescent lamps. Since the colors of the latter vary slightly with changes in ambient temperature, the variation in colorimeter response with changes in room temperature could not be tested conveniently.

Because of differences in room temperature and ventilation, results obtained on different runs are not directly comparable. The corrections to be made to "instrumental" color coordinates have been determined empirically each day by the use of standard lamps. To test the consistency of the results obtained by this method, several standard lamps of each of two types were used from three to seven times during a period of about a month. The average corrections found on any one day for lamps of a single type were applied to the "instrumental" color coordinates obtained for the individual standard lamps. The corrected color coordinates for the standard lamps should not vary from day to day. With current readings averaging about 40 percent of full scale on a Weston model 622 microammeter, the average deviation of the corrected values of x and y was 0.0007.* This figure is a measure of the accuracy which may be attained if systematic errors are eliminated by the use of standard lamps whose calibrations are sufficiently accurate. There is no reason to suppose that similar accuracy could not be attained in the rating of other sources, or of reflecting or transmitting materials, provided that suitable standards are used.

* We are indebted to Mr. H. Schoenfeldt, of our Fluorescent Lamp Department, for the data on which this figure is based.

Lumen Ratings

Since the meter reading with filter B is approximately proportional to the candlepower of the lamp in the direction of measurement, the colorimeter can serve as a photometer, also. The last line of Table II gives the ratio of the lumen output of each lamp, computed from spectral intensity data, to the current (in microamperes) furnished by the cell with the B filter. Use of the average factor, irrespective of the color of the lamp, would not cause errors greater than 4 percent. However, the factors may vary from day to day, if the instrument is sensitive to changes in room temperature.† To obtain the highest accuracy, the factors for computing lumens should be determined with the aid of standard lamps at least once each day.

Methods for Improving Instrument

The ideal instrument for routine ratings gives the desired result without computations. A meter with a 0–1.00 scale would indicate color coordinates directly if the sum of the three readings obtained with the colorimeter were exactly full-scale. To attain this condition the meter was shunted with a variable resistance and the circuits were so arranged that all the cells could be connected in parallel across the meter. To obtain approximately equal shunting action on all three circuits, the circuits containing a single cell were each provided with a 3000-ohm re-

† Our data furnish no information on this point because the lumen output of a fluorescent lamp depends, to some extent, on the ambient temperature.

sistor shunted across the cell. Nevertheless, the ratio of the current obtained with all the circuits in parallel to the sum of the three individual currents ranged from 0.83 to 0.87. Even with lamps of approximately the same color, this ratio varied about 2 percent. Consequently the reading with all circuits in parallel could not be used as a guide for setting the shunt. This condition could be remedied by use of a meter with a resistance of 20 ohms or less.

Use of a single standard lamp, regardless of the range of colors to be rated, would be permissible if the spectral sensitivity curves of the cell-filter combinations matched the $\bar{x}$, $\bar{y}$ and $\bar{z}$ curves almost perfectly. This could be attained only by the use of several components in every filter,[5] or by the preparation of special glass or gelatine filters. The latter procedure has been followed successfully[6] in matching the $\bar{y}$-curve.

Conclusions

The four-filter colorimeter described above can be adjusted to give color coordinates within 0.010 for four out of the seven colors tested. Candlepower ratings made with this instrument have systematic errors ranging up to 4 percent if a single factor is used for lamps of all colors. By calibrating with standard lamps similar to the lamps which are to be rated, the errors in color coordinates can be reduced to 0.001 and the candlepower errors can be reduced to less than one percent.

The instrument might be made direct-reading if a low resistance meter were used with it. The development of much better filters might eliminate the necessity for a standard lamp of each type that is to be rated.

[5] J. W. Perry, J. Sci. Inst. **15**, 270 (1938) reports that gelatine and liquid filters, as well as glass ones, are used in the Hilger Company "Blancometer" in order to make the cell-plus-filter sensitivities correspond, as nearly as possible, to the I. C. I. $\bar{x}$, $\bar{y}$, and $\bar{z}$ functions.

[6] O. H. Knoll and R. G. Weigel, Das Licht **8**, 39 (1938)

A Hydrogen Arc for Absorption Spectroscopy

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LIGHT sources of various types were tried in the course of studies on the absorption of ultraviolet light by certain organic liquids. For these absorption studies, Hilger notched echelon cells[1, 2] were used, adapted to a Bausch and Lomb medium size quartz spectrograph (Catalog No. 2820). Discontinuous spectra, such as are emitted by electric discharges between electrodes of iron, Chromel or tungsten, were not found satisfactory for this purpose. A continuous spectrum, such as that emitted by a high voltage hydrogen arc, was found to be more desirable but was not sufficiently intense and, not being a point source, also proved unsatisfactory. Finally, a low voltage hydrogen arc, described by Duffendack and Manley[3] and R. H. Munch,[4] was modified to meet our requirements and has been in use in our laboratory during the past four years. Arcs of this type have been furnished to other laboratories where they have met with considerable success.

The advantages of this arc over other types are: (a) It is simple to operate. (b) It is exceedingly reliable and constant in operation. (c) Its intensity is high because of its high current density. (d) The arc may be made to take the form of an approximate point or slit. (e) It is suitable for many experiments requiring a continuous spectrum in the ultraviolet region. (f) The cost is low.

[1] F. Twyman, L. J. Spencer and A. Harvey, Trans. Opt. Soc. **33**, 37 (1931–32).
[2] *The Notched Echelon Cell for Rapid Absorption Spectrophotometry* (Adam Hilger, Ltd., 1933), Hilger Pub. No. 178.
[3] O. S. Duffendack and J. H. Manley, J. Opt. Soc. Am. **24**, 222 (1934).
[4] R. H. Munch, J. Am. Chem. Soc. **57**, 1863 (1935).

Figure 1 is a schematic drawing showing the essential elements of the arc. The cathode consists of an oxide-coated filament surrounded by a

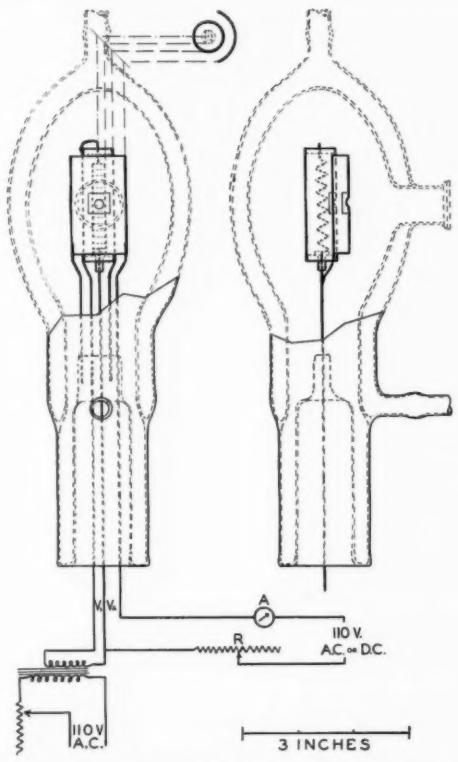

FIG. 1. Schematic drawing of low voltage hydrogen arc. V_1—Filament voltage, 3.5–4.0 volts; V_2—arc voltage, 40.0 volts; A—ammeter to measure arc current, 1.0–1.5 amperes; and R—variable resistance, 100 ohms, −2.0 amperes.

FIG. 2. (A) Spectrogram obtained with low voltage hydrogen arc, using a Hilger E31 spectrograph. (B) Mercury arc spectrum for comparison.

nickel cylinder with an orifice which can be adapted to any size or shape; the anode is a rectangular piece of molybdenum with an orifice to correspond to that of the cathode. The cathode-anode assembly is placed in a Pyrex bulb onto which is sealed a quartz window. The bulb is completely water jacketed. The filament is a strip of nickel screen approximately $\frac{1}{4}''$ wide (the exact width being 7 strands of 0.001″ nickel) and $5\frac{1}{2}''$ long, made into a corrugated form and dipped into an oxide coating material made from a 50–50 mixture of strontium and barium oxides; or, if desired, an oxide coating material which is even more satisfactory can be purchased.[5] The cathode cylinder is made of 0.010″ nickel, $\frac{9}{16}''$ in diameter and 2″ long. One terminal of the filament is insulated from the cylinder by a small flanged quartz tube. The cathode orifice used in this laboratory is a 3-mm hole in a tungsten or molybdenum sheet, spot welded into a larger hole in the nickel. A 5-mm hole is bored in the tungsten or molybdenum anode and is placed directly opposite the cathode orifice. Corresponding slit dimensions are 1 mm×8 mm and 2 mm×12 mm. The quartz window is sealed on with glyptal lacquer and thoroughly dried in a drying oven.

The electrical characteristics are indicated in Fig. 1. The filament carries a current of 10 or 12 amperes at 3.5 to 4.0 volts, (V_1), and should be heated to a dull red. As soon as the arc is started the filament current may be turned off. This will increase the life of the filament. The arc will run on either alternating or direct current, though direct current is more efficient. The arc voltage (V_2) is approximately 40 volts and is regulated by the variable resistance R, which is about 100 ohms, capable of carrying a current of 2 amperes. The arc current is measured by the ammeter A and should not exceed 1.0 ampere for continuous running or 1.5 amperes for short intervals. Larger current can be attained by increasing the dimensions of the cathode-anode assembly, enabling greater dissipation of heat.

The filling of the arc with hydrogen may be simple or complicated depending on requirements. Using ordinary tank hydrogen with a

[5] Obtainable from the Callite Products Company, Union City, New Jersey.

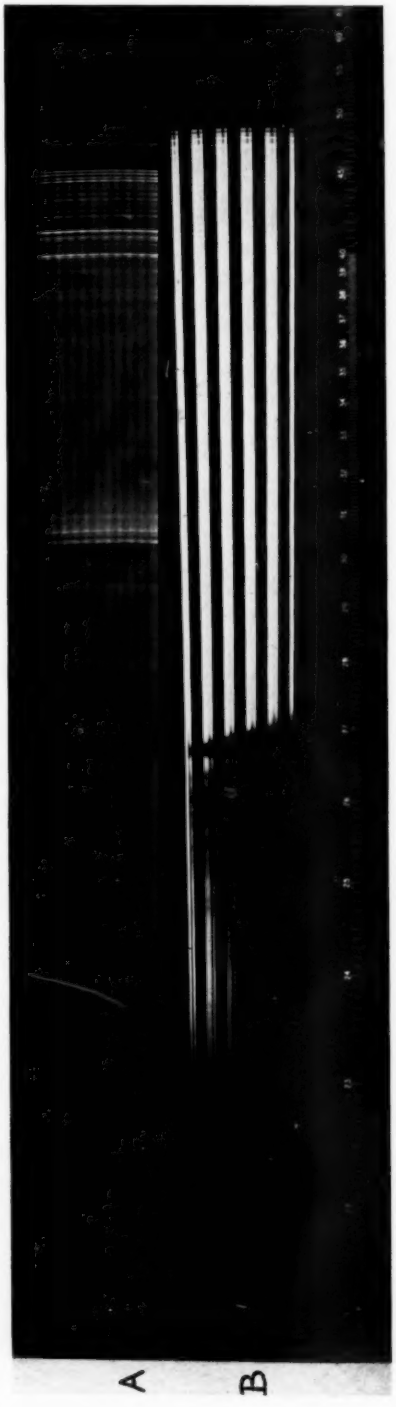

FIG. 3. (A) Spectrogram taken with Bausch and Lomb medium size spectrograph with echelon cells filled with water. Exposure 5 seconds. (B) Absorption spectrum of toluene (approximately 0.01 percent solution in alcohol.) Sector setting of 15. Exposure 1 minute. Eastman 33 plates used.

Hyvac oil pump and running, evacuating and refilling to the proper pressure a few times has been found to be a satisfactory procedure. The bulb is finally filled with hydrogen to a pressure of from 4 to 6 mm (5.5 mm being perhaps the optimum). If a high vacuum system with mercury pumps and purified hydrogen is used there will be fewer lines in the continuous spectrum; however, these lines are very useful in wavelength calibrations. In degassing, the cathode and anode should not be brought to a red heat for the nickel will become spongy and absorb hydrogen on cooling, thus altering the pressure of the hydrogen.

A photograph of the continuous spectrum produced by one of these arcs, together with that of a mercury arc for comparison is shown in Fig. 2. This picture was taken with a Hilger E31 spectrograph on Eastman No. 40 plates, $3\frac{1}{4}\times4\frac{1}{4}$, coated with Eastman ultraviolet sensitizer. The original negative shows that the hydrogen arc spectrum extends as far as 1850A. In Fig. 3 are spectrograms taken with the Bausch and Lomb spectrograph on Eastman No. 33 plates, $4''\times10''$, and using Hilger echelon cells. In (A) both cells are filled with water, and the exposure time is 5 seconds. The absorption of toluene in alcohol (approximately 0.05 percent solution) is shown in (B). With the sector setting at 15 the exposure time was one minute. The intensity of the arc is roughly comparable to that of an intense electric spark between iron electrodes and about five times more intense than a water-cooled high voltage hydrogen discharge tube used in this laboratory.

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